# Cleaning and pre-treatment procedures for biogenic and synthetic calcium carbonate powders for determination of elemental and boron isotopic compositions

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**Abstract**

In preparing calcium carbonate samples for the measurement of various geochemical proxies, it is often necessary to remove contaminating phases while leaving the phase of interest altered as little as possible. Here we evaluate the effects of some common cleaning protocols (rinsing ($H_2O$), bleach (~3% NaOCl), hydrogen peroxide (30%), sodium hydroxide (0.006 – 0.1 M NaOH), and acid leaching (0.05 N $HNO_3$)) on the elemental (Li, B, Na, Mg, Sr, Ba, Pb, and U) and boron isotope composition of both biogenic and synthetic calcium carbonates formed in marine environments.

In untreated samples, the presence of elevated concentrations of Na and Mg, the most abundant cations in seawater, can be reduced with minimal cleaning (e.g. rinsing). Cleaning protocols that cause partial dissolution are problematic, especially for samples that are compositionally heterogeneous because the remaining sample may be biased towards particular phases with distinctive elemental or isotopic compositions. We show

46 that the use of either acid or unbuffered hydrogen peroxide can lead to partial dissolution
47 which was associated with an increase in the U/Ca ratio of the remaining sample.
48 Bleaching or rinsing with water did not result in significant sample dissolution,
49 suggesting these cleaning techniques may be safely used on heterogeneous samples.
50 Cleaning treatments, other than those resulting in significant dissolution of heterogeneous
51 samples, had no significant effect on $\delta^{11}B$, suggesting that boron isotopes are generally
52 robust to the effects of sample pre-treatment.
53

54 **1. Introduction**

55 The elemental and isotopic compositions of a wide range of marine calcium carbonates
56 provide insight into mineralization processes (e.g. Elderfield et al., 1996; Allison and
57 Finch, 2010; McCulloch et al., 2012) and are used as proxy records of environmental
58 conditions (e.g. Montagna et al., 2007; LaVigne et al., 2008; Saenger et al., 2008; Zinke
59 et al., 2014). In order to interpret elemental and isotopic compositions, it is critical to
60 ensure that measurements reflect the carbonate material of interest and not a
61 contaminating phase. Marine samples are particularly susceptible to contamination from
62 residual seawater, and biologically deposited materials may contain organic matter which
63 can retain a wide range of elements (Amiel et al., 1973a,b; McConchie and Harriott,
64 1992; Mohnen 2008; Blanco-Ameijeiras et al., 2012). In some cases, secondary
65 precipitates may form after the initial material of interest was deposited, surfaces may
66 become enriched in certain elements as a result of adsorption, and particles present in the
67 environment may become mixed with or even incorporated into the sample (Barnard et
68 al., 1974; Macintyre et al., 1976; Shen and Boyle 1988; Millero et al., 2001; Nothdurft et

69 al., 2005). A wide range of cleaning protocols has been developed to remove many of
70 these sources of contamination (Table 1).
71
72 Critical to any cleaning method is the need to not only remove contaminating phases, but
73 also to leave the material of interest as pristine as possible. Although many cleaning
74 methods have been extensively tested on samples collected from the natural environment,
75 less attention has been devoted to testing cleaning methods on nominally 'clean'
76 materials, (i.e. free from biologically produced organic compounds) to assess the
77 potential for the cleaning protocol to result in the loss of sample or alter compositionally
78 heterogeneous samples. A brief summary of the methods which have been previously
79 tested and the parameters measured is given in Table S1. Unfortunately no cleaning
80 technique is universally applicable for all trace element measurements, and very few
81 studies have addressed the effects of cleaning on $\delta^{11}B$ (Table S1).
82
83 In this study, we used synthetic aragonite precipitated from filtered seawater as well as
84 biogenic samples. For synthetic materials seawater is the most likely contaminant, while
85 seawater and residual organic materials are likely sources of contamination in biogenic
86 samples. Unique to our study is the use of compositionally zoned synthetic aragonite
87 powders, which avoids the complication posed by tissue contamination. This provides an
88 opportunity to assess whether organic removal steps affect aragonite independent of
89 effects from tissue residues. We also give special attention to the effects of cleaning
90 protocols on boron isotopes in both 'clean' and 'organic-rich' samples, an issue that has
91 to date received relatively little attention.

92 Table 1. Potential contaminants encountered in marine calcium carbonate samples,
93 methods/reagents for their removal, and example references for each. See Table S1 for a
94 summary of studies which have compared different cleaning approaches.

| Contaminant | Cleaning method | References |
|---|---|---|
| Particulate | Manual removal | Barker et al., 2003; van de Flierdt et al., 2010 |
| | Suspension in water/methanol | Boyle and Keigwin, 1985; Barker et al., 2003 |
| Oxides | Reductive cleaning - $NH_2OH{\cdot}HCl$ and $NH_4OH$ | Boyle, 1981; Blanco-Ameijeiras et al., 2012 |
| | Reductive cleaning - hydrazine and ammonium citrate | Boyle and Keigwin, 1985; Shen and Boyle, 1988 |
| Barite | chelation with alkaline diethylene-triaminepentaacetic acid (DTPA) | Lea and Boyle, 1993 |
| Adsorbed ions | Rinsing | Amiel et al., 1973; Mitsuguchi and Kawakami, 2012 |
| | Weak acid | Shen and Boyle, 1988; Lea and Boyle, 1993; Rosenthal et al., 1997 |
| | Buffers – acetate | Amiel et al., 1973; Tessier et al., 1979; Wang et al., 2013b |
| | Chelating agents – EDTA | van de Flierdt et al., 2010 |
| Organic | Oxidation with $H_2O_2$ | Sinclair, 2005; Armid et al., 2011; Mitsuguchi and Kawakami, 2012 |
| | Oxidation with $H_2O_2$ and NaOH | Boyle and Keigwin, 1985; Tudhope et al., 1996; Blanco-Ameijeiras et al., 2012 |
| | Oxidation with $H_2O_2$ and $HClO_4$ | Cheng et al., 2000 |
| | Oxidation with $H_2O_2$ and $NH_4OH$ | Foster et al., 2013 |
| | Oxidation with $H_2O_2$ and $(NaPO_3)_6$ | Hart et al., 1997 |
| | Oxidation with $H_2O_2$ and $Ca(OCl)_2$ | Fang and Chou, 1992 |
| | Oxidation with $H_2O_2$ and NaOCl | Bairbakhish et al., 1999 |
| | Oxidation with NaOCl | St. John, 1974; Sanyal et al., 1996; Tudhope et al., 1996; Clode and Marshall, 2003 |
| | Heat (with or without $O_2$) | Fabry and Delaney, 1989; Abu-Hilal, 1994; Robinson et al., 2004; Wierzbowski, 2007 |
| | Hydrolysis - NaOH | Young, 1971; Pingitore et al., 1993; Clode and Marshall, 2003 |

| | | |
|---|---|---|
| | $NaClO_3$ | Allison et al., 2010 |
| | TMAH (tetramethylammonium hydroxide) | Stoll et al., 2001 |

## 2. Methods

### *2.1. Carbonate samples*

Cleaning protocols were tested on a variety of calcium carbonate samples (Table 3). Samples included relatively clean coral powders derived from *Porites* sp.: NEP, an in-house coral standard derived from a coral core collected from New Ireland (2.5°S, 150.5°E), Papua New Guinea (Alibert and Kinsley 2008), and the inter-laboratory coral standard JCp-1 (Okai et al., 2002). Organic-rich samples included a specimen of *Marginopora vertebralis* (a high Mg-calcite foraminifera) cultured at the University of South Pacific (Fiji) and a sample taken from the tissue zone of a massive *Porites* sp. coral collected from Myrmidon Reef (18.3°S, 147.4°E), Great Barrier Reef, Australia. Both organic-rich samples were dried following collection without any treatment to remove the tissue, thus organic material from the organism remained associated with the calcium carbonate. To test the effects of sample dissolution, compositionally heterogeneous synthetic aragonite samples grown at Woods Hole Oceanographic Institution (WHOI) (see section 2.1.1) were used. A wide range of other biogenic and synthetic aragonite powders from various sources were also used to test the effects of specific cleaning steps on elemental ratios. Samples not already in the form of a powder were ground into a powder using an agate mortar prior to being used for cleaning tests.

#### *2.1.1. Synthetic aragonite*

116 Two synthetic aragonite samples were used for the bulk of the protocol tests. These were
117 prepared by dissolving 3.67 g $CaCO_3$, 0.0484 g $SrCO_3$, and 17.91 g $MgCl_2$ in 4.105 kg
118 filtered seawater at ~ 1 atm (~101 kPa) $pCO_2$. The final solution was passed through a
119 0.45 μm filter to remove any undissolved particles. A mass of 656.8 ± 0.7 g of filtered
120 solution was added to ~1L PET containers (SOLO) held within a constant temperature
121 bath (25.15°C). Solutions were stirred continuously at 130 rpm with a magnetic stir bar
122 and bubbled with air at either 5 (precipitate 1/19/11 e) or 10 (precipitate 1/19/11 d)
123 ml/min (see supplemental material for further details). Shortly after the start of
124 precipitation (as inferred from initial declines in pH and alkalinity – see Fig. S1), a $^{87}Sr$
125 spike was added (per Holcomb et al., 2013) to more than double the $^{87}Sr$ concentration,
126 while near the end of the experiment a $^{86}Sr$ spike was added to the solution. Experiments
127 were terminated by collecting the precipitate on a 0.7 μm glass fiber filter, rinsing with
128 distilled water and ethanol, and then air drying the precipitate. The aragonitic
129 composition of the precipitate was confirmed with raman microscopy (per Holcomb et
130 al., 2009).
131 Additional synthetic aragonites prepared using a range of protocols (e.g. Kitano et al.,
132 1978; Holcomb et al., 2009; Gabitov et al., 2011; Wang et al., 2013a) were also used to
133 test cleaning protocols, all having been rinsed with $H_2O$ and ethanol at the time of
134 collection. Due to the nature of the experiments, all the synthetic aragonites used are
135 expected to be compositionally heterogeneous (e.g. Gaetani and Cohen, 2006; Holcomb
136 et al., 2009), and for experiments spiked with isotope spikes, there are specific Sr isotope
137 heterogeneities corresponding to known time points in the precipitation experiments.
138

139 *2.2. Cleaning protocols*

140 From the range of existing cleaning methods, we chose five principal cleaning methods to
141 test: rinsing ($H_2O$), acid washing ($HNO_3$), bleaching (sodium hypochlorite, NaOCl or
142 equivalently NaClO), oxidation with hydrogen peroxide ($H_2O_2$), and hydrolysis (NaOH).
143 Even for these five reagents, there are multiple different implementations which have
144 been used in the literature, covering a wide range of reagent strengths, pHs, durations,
145 and temperatures, only a small subset of which were chosen for testing in the current
146 study. Published protocols include $H_2O$ treatments ranging from brief rinses to more than
147 a day (e.g. Allison 1996; Grottoli et al., 2005; Henehan et al., 2013), bleach treatments
148 from ~3 -12% NaOCl (e.g. Allison 1996; Leder et al., 1996; Clode and Marshall 2003;
149 Ingalls et al., 2003), treatment with acids from <0.001 - 0.2 N (e.g. Rosenheim et al.,
150 2004; Brock et al., 2010; Henehan et al., 2013), $H_2O_2$ treatments at concentrations from
151 <1 - >30% (McConchie and Harriott 1992; Grottoli et al., 2005; Reynaud et al., 2007;
152 Armid et al., 2011; Henehan et al., 2013), and with NaOH <0.1 -~6 N (e.g. Watanabe et
153 al., 2001; Clode and Marshall 2003; Tambutte et al., 2007; Krause-Nehring et al., 2011).
154 We chose treatments from within the range of published concentrations and durations for
155 testing. A sub-set of the experiments were conducted at the University of Western
156 Australia and the rest at Woods Hole Oceanographic Institution. The different protocols
157 used and samples tested are summarized in Tables 2 and 3.
158

159 Table 2. Steps for each cleaning protocol tested. General information relating to multiple
160 protocols is given in section 2.2.1.

| Protocol | Steps |
|---|---|

| | |
|---|---|
| 1 (bleach) | 2-4x $H_2O$ rinse, 1x 1-2 mL of 3-7% NaOCl for 15 min including 5 min of sonication, 5-6x $H_2O$ rinses including a few seconds of sonication |
| 2 (acid) | protocol 1 followed by 0.5 mL of 0.05 N $HNO_3$ for 15 min including 5 min of sonication, 5x $H_2O$ rinses |
| 3 ($H_2O_2$) | 2-4x $H_2O$ rinse, 1x 1-2 mL of 30% $H_2O_2$ for 15 min including 5 min of sonication, 5x $H_2O$ rinses including a few seconds of sonication |
| 4 (rinsing) | 2-4x ~4 mL $H_2O$ rinse |
| 5 (sonication) | 1 mL $H_2O$ for 15 min including 5 min sonication, 4x $H_2O$ rinse |
| 6 (bleach x2) | 2x $H_2O$ rinse, 2x 1-2 mL of 3-7% NaOCl for 30 min including 15 min of sonication, 5x $H_2O$ rinses including a few seconds of sonication |
| 7 (NaOH) | 2x $H_2O$ rinse, 1x 2 mL 0.03 – 0.07 M NaOH for 15 min including 5 min sonication, 5x $H_2O$ rinses including a few seconds of sonication |
| 8 ($HNO_3$ + bleach) | 2x $H_2O$ rinse, 1x 0.5 mL of 0.05 N $HNO_3$ for 15 min including 5 min of sonication, followed by protocol 1 |
| 9 (hot acid) | dissolution in a few drops of ~14 N $HNO_3$, incubated 2 d on a 90 $^oC$ hotplate |
| 10 (rinse) | 3x $H_2O$ rinse |
| 11 (NaOH) | 2x 0.02 M NaOH, 2x $H_2O$ rinse |
| 12 (NaOH) | 3x 0.006 – 0.1 M NaOH, 3x $H_2O$ rinse |
| 13 (bleach) | 3x 3% NaOCl, 3x $H_2O$ rinse |

161

Table 3. Samples analyzed, the minimum number of replicate samples used per protocol, cleaning protocols compared (as detailed in Table 2, sequential protocols are indicated by '+'), elements/isotopes measured, laboratory carrying out the analysis, and where the results are shown.

| Sample, # replicates | Cleaning protocols | Measurements | Lab | Results |
|---|---|---|---|---|
| coral (NEP), 3x | none, 1, 2 | $\delta^{11}$B, Li, B, Na, Mg, Sr, Ba, U | UWA | Fig. 1, 2 |
| coral w organics (massive *Porites*), 1x | none, 1, 4, 6, 9 | $\delta^{11}$B, Mg, Sr, Ba, U | UWA | Fig. 1, S3, section 3.2.4 |
| corals (various), 4x | 1, 1+7, 8 | $\delta^{11}$B, Li, B, Na, Mg, Sr, Ba, Pb, U | UWA | Fig. 5, section 3.2.3 |
| coral (JCp-1), 14x | none, 1 | $\delta^{11}$B | UWA | Fig. 1 |
| foraminifera w organics, 2x | 1, 3, 4 | $\delta^{11}$B, Li, B, Na, Mg, Sr, Ba, U | UWA | Fig. 1, S2 |
| synthetic aragonite 1/19/11 d, 3x | none, 1, 3, 4, 5 | $\delta^{11}$B, Li, B, Na, Mg, Sr, Ba, Pb, U | UWA | Fig. 1, 4 |
| synthetic aragonite 1/19/11 e, 3x | none, 1, 2 | $\delta^{11}$B, Li, B, Na, Mg, Sr, Ba, Pb, U | UWA | Fig. 1, 3 |
| synthetic aragonite TS3, 3x | 1, 4, 7 | B, Na, Mg, Ca, Sr, Ba, Pb, U | UWA | Fig. S4 |
| synthetic aragonites (various), 26x | 10, 11 | Mg, Sr, Ba, U | WHOI | section 3.2.2 |
| synthetic aragonite TS3, 3x | 10 x3, 10+12, 11, 10+13 | Mg, Sr, Ba, U | WHOI | Fig. S5 |

*2.2.1. Cleaning steps*

All treatments carried out at UWA (protocols 1-9) were carried out in a clean room (McCulloch et al., 2014). Sub-samples (~5-20 mg depending on the sample type) of each of the powders were weighed in pre-cleaned, pre-weighed polypropylene tubes (5 mL capacity). At least two sub-samples of each sample type were assigned to a given treatment, except for treatment 9 (Table 3). In addition to samples, empty tubes were also processed as if they were samples to check procedural blanks. During each step of the protocol samples were shaken vigorously during exposure to the given cleaning

175 agent. All cleaning steps were carried out at room temperature (~21 $^{o}$C), unless specified
176 otherwise. To separate the powder from the cleaning agent, tubes were centrifuged at
177 ~3000 rcf for 30 – 120 s, depending on the sample, prior to removing the supernatant.
178 Sonication steps were carried out in an Unisonics ultrasonic bath. Water (18 MΩ) came
179 from a Milli-Q Integral 5 unit fitted with progaurd TS2 and quantum cartridges
180 (Millipore). Reagents used included ~6 - 14% NaOCl solutions (Merck 105614 or Rowe
181 CS12345), 30% $H_2O_2$ solution (Rowe CH2852 CC070711), NaOH (Rowe CS12613),
182 $HNO_3$ was distilled from analytical grade $HNO_3$ using a Teflon subboiling distillation
183 system (Savillex DST-1000). Once cleaning was completed, tubes were lightly capped
184 and samples dried by placing them on a 60-70$^{o}$C hotplate with a heat-lamp above the
185 hotplate to keep the tops warm. Tubes were weighed periodically until the weight
186 stabilized, indicating that the sample was dry.
187
188 Treatments carried out at WHOI (Table 3) used 0.75 mL volumes of wash/rinse solutions
189 and ~100 μg powder. All processing was carried out in polypropylene 1.5 mL
190 microcentrifuge tubes. Samples were suspended, centrifuged at 10,000 rpm for 2 minutes,
191 and the supernatant pipetted off. Post cleaning, samples were dried in open
192 microcentrifuge tubes placed in a laminar flow hood. Water used for rinsing and
193 preparing reagents was deionized (18 MΩ, Millipore), $HNO_3$ was trace metal grade
194 (Fisher A509-p212, lot# 1112110), NaOH was from Fisher (975017), and NaOCl was
195 laboratory grade (Fisher ss290).
196
197 *2.3. Measurements*

198 *2.3.1. UWA*

199 Samples were dissolved in $HNO_3$ (~0.08 N final acid strength) by adding ~0.5 N $HNO_3$
200 directly to the sample (in the same tube used for cleaning steps). Solutions were used
201 directly for boron purification (section 2.3.1.1) or diluted in 2% $HNO_3$ spiked with ~19
202 ppb Sc, 19 ppb Y, 0.19 ppb Pr, and 0.095 ppb Bi (note 19 ppb V was also included
203 initially, however its use was discontinued in favor of just using Sc for correcting Ca
204 intensities) for trace element measurements. Most trace element measurements were
205 made on ~10 ppm (~0.25 mM) Ca solutions, however to improve measurement precision
206 of $^{7}Li$, $^{11}B$, and $^{208}Pb$, some samples were also measured at ~100 ppm (~2.5 mM) Ca –
207 details of which samples were measured at which concentration are given in the
208 supplementary data table.
209
210 Trace element measurements were made using a Q-ICP-MS (X-series II, ThermoFisher
211 Scientific) using the standard Xt interface and plasma screen. During measurement,
212 samples were placed in an autosampler (Elemental Scientific SC4 DX). Sample was
213 introduced by a teflon microflow nebulizer (Elemental Scientific PFA-ST) using a 100
214 µL/min capillary to a quartz spray chamber chilled to 2°C (Elemental Scientific PC3).
215 The nickel cones of the mass spectrometer were preconditioned for a minimum of 30
216 minutes with either a 10 or 100 ppm Ca (matching the sample concentration to be
217 measured) solution in 2% $HNO_3$ prior to starting measurements. Analyses were carried
218 out in peak-hopping pulse counting mode. Wash-out was 20 s and uptake 100 s per
219 sample; 2% $HNO_3$ was used as the wash solution between samples. Measurements used

100 sweeps with 3-10 repetitions (blank measurements were made using fewer repetitions than samples or standards) for all measured elements.

Synthetic standards for trace element analysis were prepared from HPS standard solutions and used to check measurement reproducibility. A laboratory coral standard (*Porites* sp. collected from Davies Reef, Great Barrier Reef, Australia (147.7 $^{o}$E, 18.8 $^{o}$S)) and JCp-1 (Okai et al., 2002) were measured periodically throughout a run to standardize measurements. Values for the Davies Reef coral were based on repeated measurements against the JCp-1 coral standard. Elemental ratios (mmol/mol) used for JCp-1 were as follows: 0.006185 Li/Ca, 0.4596 B/Ca, 19.83 Na/Ca, 4.199 Mg/Ca, 8.838 Sr/Ca, 0.007465 Ba/Ca, 0.00009106 Pb/Ca, 0.001192 U/Ca based on Okai et al., (2002), Inoue et al., (2004, 2009), and Hathorne et al., (2013). For the Davies Reef coral: 0.00633 Li/Ca, 0.53 B/Ca, 19.8 Na/Ca, 4.674 Mg/Ca, 8.95 Sr/Ca, 0.003965 Ba/Ca, 0.000126 Pb/Ca, and 0.001096 U/Ca. Measured counts for each element were corrected (background subtraction) for background counts (measured on 2% $HNO_3$ for correcting counts of spiked elements, or on the spike solution for correcting other elements). Expressed as a percentage of typical sample signal intensities, for 10 ppm Ca solutions blank values were: 17% $^{7}$Li, 22% $^{11}$B, 0.5% $^{23}$Na, 2% $^{24 \text{ or } 25}$Mg, <0.1% $^{43}$Ca, 0.1% $^{45}$Sc, 3% $^{84}$Sr, 0.1% $^{86}$Sr, <0.1% $^{87}$Sr, <0.1% $^{88}$Sr, <0.1% $^{89}$Y, 2% $^{138}$Ba, <0.1% $^{141}$Pr, 25% $^{208}$Pb, 0.1% $^{209}$Bi, <0.1% $^{238}$U; and for 100 ppm Ca solutions, blank values were: 0.5% $^{7}$Li, 5% $^{11}$B, 0.2% $^{25}$Mg, 0.1% $^{45}$Sc, 1% $^{46}$Ca, <0.1% $^{84}$Sr, <0.1% $^{89}$Y, 0.1% $^{138}$Ba, <0.1% $^{141}$Pr, 5% $^{208}$Pb, 0.1% $^{209}$Bi, <0.1% $^{238}$U.

Spikes were used to correct for variations in instrumental mass bias for the measured elements closest in mass to a given spike. To calculate sample ratios, count ratios from

two bracketing standards were used, drift between standards was assumed to occur linearly with time. Reproducibility, expressed as percent relative standard deviation (%RSD), for coral standards measured during the analytical runs for which data are presented here was: 4 Li/Ca, 4 B/Ca, 0.5 Na/Ca, 1 Mg/Ca, 0.1-0.4 for Sr/Ca (depending upon the isotope measured), 1 Ba/Ca, and 1 U/Ca.

2.3.1.1 Boron isotopes

Boron was purified using either cation (Bio-Rad AG50W-X8 200-400 mesh) or cation and anion (Bio-Rad AG1-X8 100-200 mesh) exchange resins to adsorb ions from the sample matrix while allowing boric acid to pass through the resin (Holcomb et al., 2014; McCulloch et al., 2014). Measurements were carried out using MC-ICP-MS as described by Holcomb et al. (2014) and McCulloch et al. (2014) using both direct injection and spray chamber introduction systems on either a Neptune Plus (ThermoFisher Scientific) or Nu (Nu Instruments) MC-ICP-MS. Sample measurements were bracketed by SRM-951 or an in-house standard (UWA24.7) in concentration-matched $HNO_3$ (~0.15 N for most samples). All data are expressed relative to SRM-951. Long-term reproducibility of coral standards was ~0.3‰ (2 standard deviation). For a given sample type, the same extraction and measurement approach was applied to all samples.

*2.3.2. WHOI*

Samples measured at WHOI were dissolved in 5% $HNO_3$ to a final concentration of approximately 40 ppm Ca. Counts of $^{24}Mg$, $^{48}Ca$, $^{88}Sr$, $^{138}Ba$, and $^{238}U$ were measured in low resolution mode on a magnetic sector ICP-MS (Thermo-Finnegan Element2) with 30

scans per sample. Between samples, the sample introduction system was washed for 3 min with 5% $HNO_3$. Measured counts were background corrected (background subtracted) based on measurements of 5% $HNO_3$. Counts were converted to elemental ratios based on measurements of JCp-1. Reproducibility, expressed as %RSD, for coral consistency standards was: 1 Mg/Ca, 0.4 Sr/Ca, 0.8 Ba/Ca, and 0.8 U/Ca.

*2.4. Statistics*

One-way ANOVAs or t-tests were used to detect significant ($p<0.01$) differences among treatments. Homogeneity of variance assumptions were not always met, however sample sizes were generally similar among treatments. When significant differences were detected with ANOVA, individual treatments were compared using a Scheffe multiple comparison procedure. Test statistics are expressed as $t_y$ or $F_{x,y,}$ where x is the treatment degrees of freedom and y is the error degrees of freedom. For treatments where more than ten replicates were made, Grubb's test for outliers was used to identify outliers which were removed from the data prior to further statistical testing. Statistical tests were carried out using the software packages SYSTAT version 9 and SAS version 7.2. Values are reported as mean ± 2 standard error. Data are provided in a supplemental .xls file.

**3. Results:**

*3.1. Boron isotopes*

289 Different cleaning protocols resulted in no significant change in $\delta^{11}B$ values for most
290 samples (Fig. 1). Only for one synthetic aragonite (1/19/11 e) were there significant
291 differences among treatments (one-way ANOVA $F_{2,6}=14.8$, $p<0.005$), with the acid
292 treated samples having lower $\delta^{11}B$ than untreated or bleached samples.

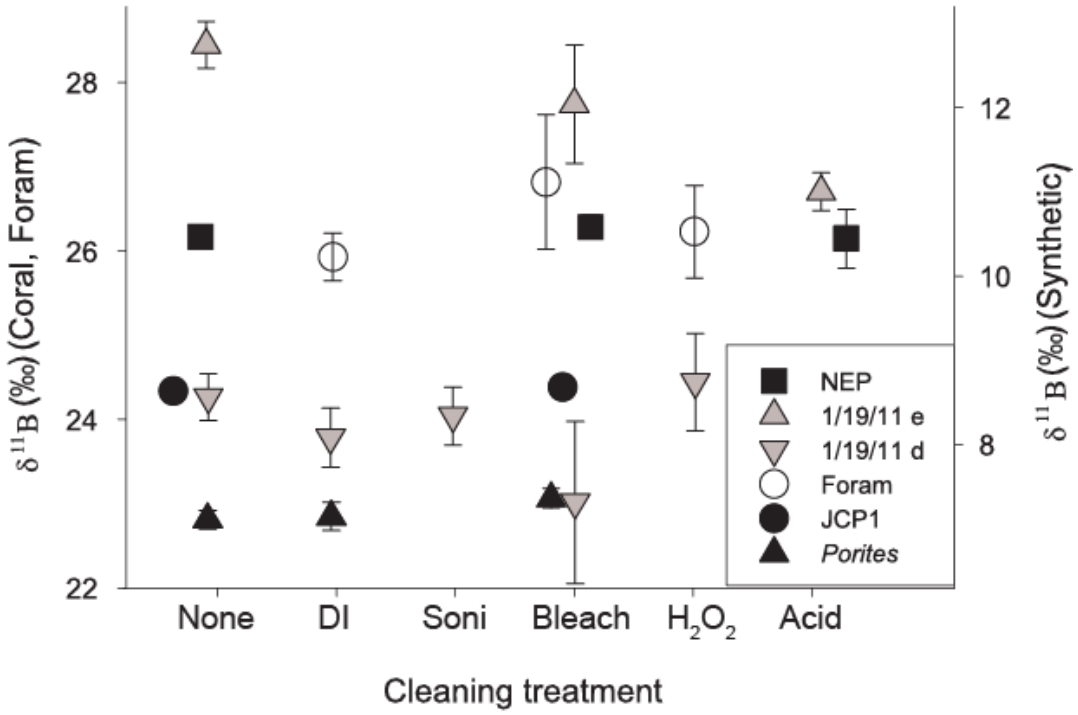



Figure 1. $\delta^{11}B$ values for different samples (coral powders: NEP, JCp-1, and *Porites* sp. contaminated with tissue, synthetic aragonites (1/19/11 d and 1/19/11 e), and a foraminifera (*M. vertebralis*) contaminated with tissue) prepared with different cleaning protocols. Cleaning protocols used were: untreated (None), rinsed with water (DI), sonicated during water rinse (Soni), NaOCl (Bleach), hydrogen peroxide ($H_2O_2$), and leaching in 0.05 N $HNO_3$ (Acid). Synthetic aragonites are plotted against the right hand axis, corals and foraminifera on the left hand axis. Symbols represent means, error bars are 2 standard errors for cleaning replicates; in some instance the error bars are not visible as they are smaller than the symbol.

304 *3.2. Trace elements*

305 *3.2.1 'Clean' aragonite*

306 Cleaning the NEP coral powder (Fig. 2) or synthetic aragonite powders (1/19/11 e (Fig.
307 3), or 1/19/11 d (Fig. 4)) resulted in no significant pair-wise differences in Li/Ca, Ba/Ca,
308 and Sr/Ca (excluding spiked isotopes) ratios. Ratios for $^{86}$Sr/Ca and $^{87}$Sr/Ca differed
309 amongst treatments for synthetic aragonite 1/19/11 d ($F_{4,10}$=8.8, $p<0.005$, and $F_{4,10}$=4.8,
310 $p=0.02$ respectively), with peroxide treated samples tending to have lower $^{86}$Sr/Ca and
311 higher $^{87}$Sr/Ca values than other treatments (Fig. 4). Acid treatment of synthetic
312 aragonite 1/19/11 e also resulted in a significant decline in $^{86}$Sr/Ca ($F_{2,6}$=41.3, $p<0.0005$,
313 pair-wise $p<0.01$, Fig. 3). For the synthetic aragonite treated with peroxide (1/19/11 d),
314 significantly higher Pb/Ca ratios were found following peroxide treatment ($F_{4,10}$= 37.9,
315 $p<0.0001$, pair-wise $p<0.0005$). Although not significant, acid treatment of synthetic
316 aragonite 1/19/11 e also tended to increase Pb/Ca ratios. A similar pattern was observed
317 with U/Ca ratios with acid treated samples having significantly higher values than other
318 treatments (ANOVA, $F_{2,5}$=200, $p<0.0001$ for NEP, $F_{2,6}$=129, $p<0.0001$ for 1/19/11 e).
319 For 1/19/11 d U/Ca ratios differed significantly among treatments ($F_{4,10}$=14.6, $p<0.0005$),
320 with bleached samples having significantly lower values than peroxide or sonication
321 treatments ($p<0.005$), as well as tending to be lower than DI washed and untreated
322 ($p<0.05$) samples.

323 All cleaning protocols led to reductions in Mg/Ca ($F_{2,6}$=434, $p<0.0001$ for NEP,
324 $F_{2,6}$=375, $p<0.0001$ for 1/19/11 e, $F_{4,10}$=811, $p<0.0001$ for 1/19/11 d) and Na/Ca
325 ($F_{2,6}$=355, $p<0.0001$ for NEP, $F_{2,6}$=2045, $p<0.0001$ for 1/19/11 e, $F_{4,10}$=506, $p<0.0001$ for
326 1/19/11 d) relative to untreated samples. For the synthetic aragonite 1/19/11 d there were

327 further significant differences amongst treatments: treatment with bleach or hydrogen
328 peroxide resulted in significantly lower Mg/Ca and Na/Ca ratios ($p<0.005$) than samples
329 that were only rinsed regardless of whether or not samples were sonicated during rinsing.
330 Further samples that were bleached had significantly higher ($p<0.005$) Mg/Ca ratios than
331 samples treated with peroxide, however Na/Ca values were not significantly higher.
332 For both synthetic aragonite samples (1/19/11 d, e), B/Ca ratios were lower in cleaned
333 ($F_{2,6}=13.0$, $p<0.01$ for 1/19/11 e, $F_{4,10}=21.7$, $p<0.0001$ for 1/19/11 d) relative to untreated
334 samples
335
336 *3.2.2. Importance of rinsing*
337 For all treatments discussed in section 3.2.1, samples were initially rinsed prior to the use
338 of other cleaning agents, primarily to reduce the possibility of soluble ions precipitating
339 out when exposed to cleaning agents, particularly basic cleaning agents. To test whether
340 this was needed, synthetic aragonite samples were either rinsed or exposed directly to
341 NaOH (without prior rinsing). Two outliers (Grubbs outlier test) were removed from the
342 dataset for each of Mg/Ca, Ba/Ca, and Sr/Ca. Relative to samples rinsed with $H_2O$,
343 samples treated with NaOH without prior rinsing were enriched in Mg/Ca (16% ±4,
344 $t_{23}=8.1$, $p<0.001$), Sr/Ca (4.2% ±0.4, $t_{23}=19.1$, $p<0.001$) and Ba/Ca (18% ±3, $t_{23}=11.2$,
345 $p<0.001$), but depleted in U/Ca (-13% ±2, $t_{25}=-10.1$, $p<0.001$).
346
347 *3.2.3. Using multiple reagents*
348 Acidic reagents tended to lead to enrichment of elements such as U and Pb (section
349 3.2.1), whereas basic reagents tended to result in lower values for those same elements

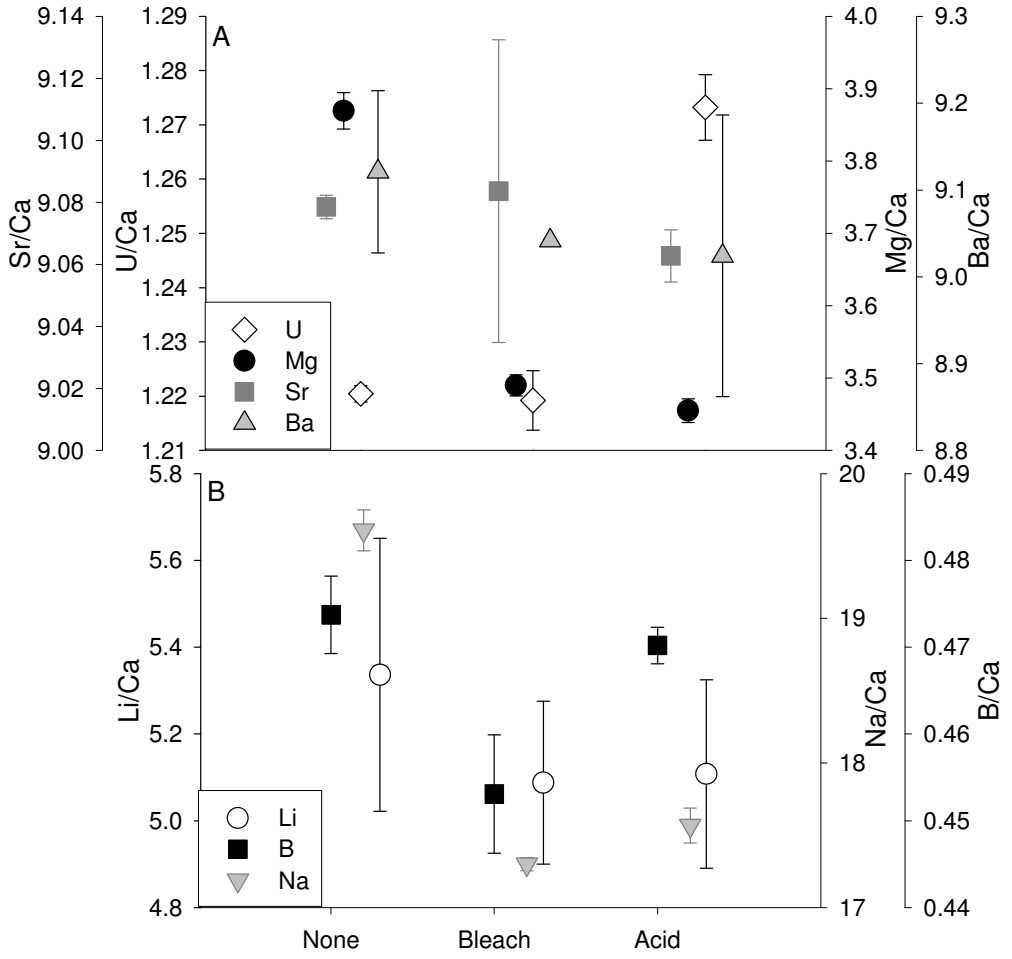
(section 3.2.1, 3.2.2). To test whether enrichment caused by acid treatment could be reversed with subsequent bleaching, several coral samples were either bleached, or treated with acid followed by bleach. The use of an acid wash step prior to bleaching resulted in a slight but significant increase in Na/Ca ($t_{14}$=4.9, p<0.001), and a decrease in Ba/Ca ($t_{14}$=-4.7, p<0.001), Pb/Ca ($t_{14}$=-10.6, p<0.001), and U/Ca ($t_{14}$=-4.3, p<0.001) relative to samples exposed to bleach alone. Other ratios were not significantly affected (Fig. 5), nor was $\delta^{11}B$ (acid washed values were 0.16±0.13 lower n=9).

To test whether the effect of basic reagents was cumulative, some samples were either bleached, or bleached and then treated with NaOH. No significant change in isotopic or elemental ratios were detected following NaOH treatment of bleached samples (Fig. 5, $\delta^{11}B$ reduced by 0.11 ±0.26, n=4).

*3.2.4. Samples with organic matter*

In the high-Mg calcite foraminifera containing organic matter, Mg/Ca exhibited modest differences among treatments ($F_{2,3}$=13.0, p<0.05), with rinsed samples having slightly higher (p<0.05) values than peroxide treated samples (Fig. S2). Na/Ca differed significantly among treatments ($F_{2,3}$=49.1, p=0.005), with peroxide treated samples having lower values than either of the other treatments (p<0.05). No significant differences among treatments were detected for Sr/Ca, Ba/Ca, Li/Ca, B/Ca, Pb/Ca, or U/Ca.

371

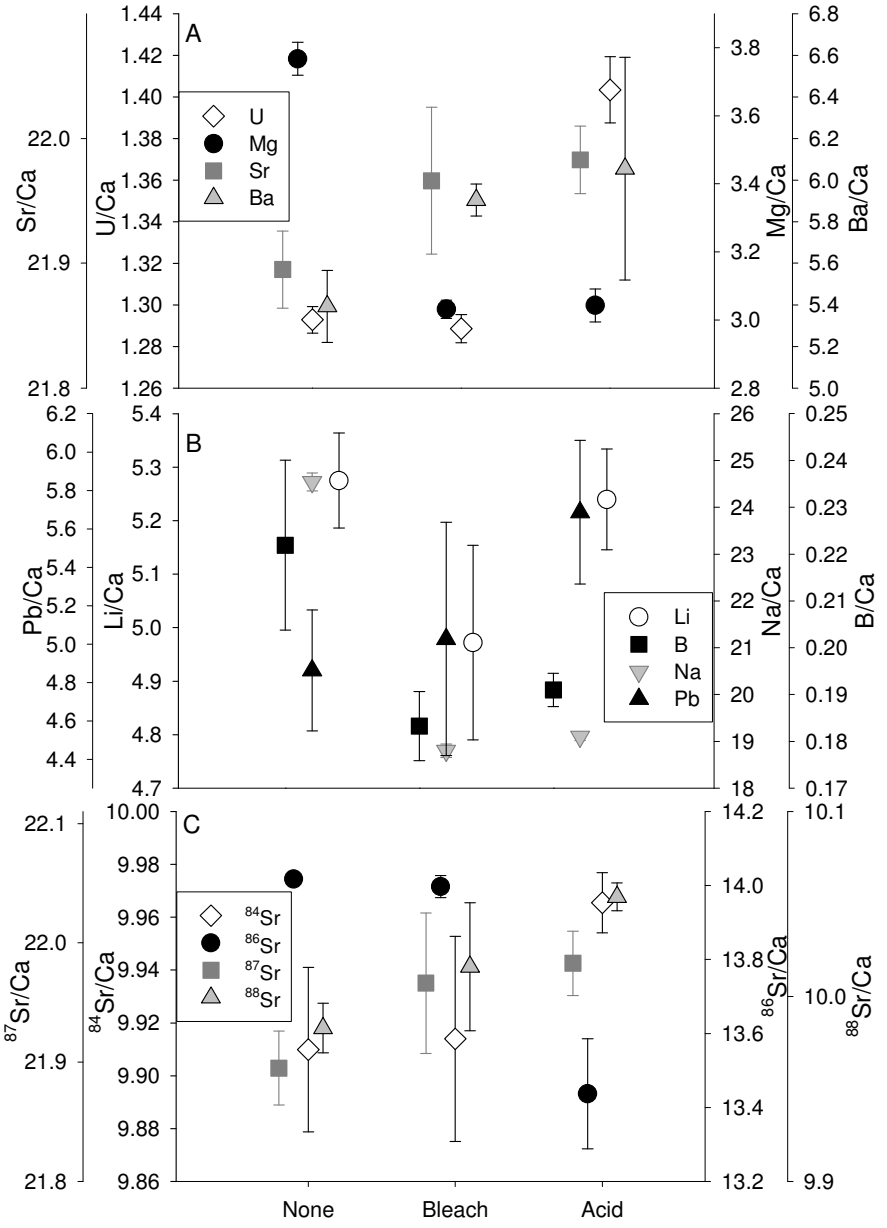



372

373 Figure 2. Element ratios for NEP coral powder prepared with different cleaning

374 protocols. Values are mmol Sr, Mg, Na, and B, or µmol U, Ba, and Li per mol Ca,

375 symbols are means, error bars are 2 standard errors.




376

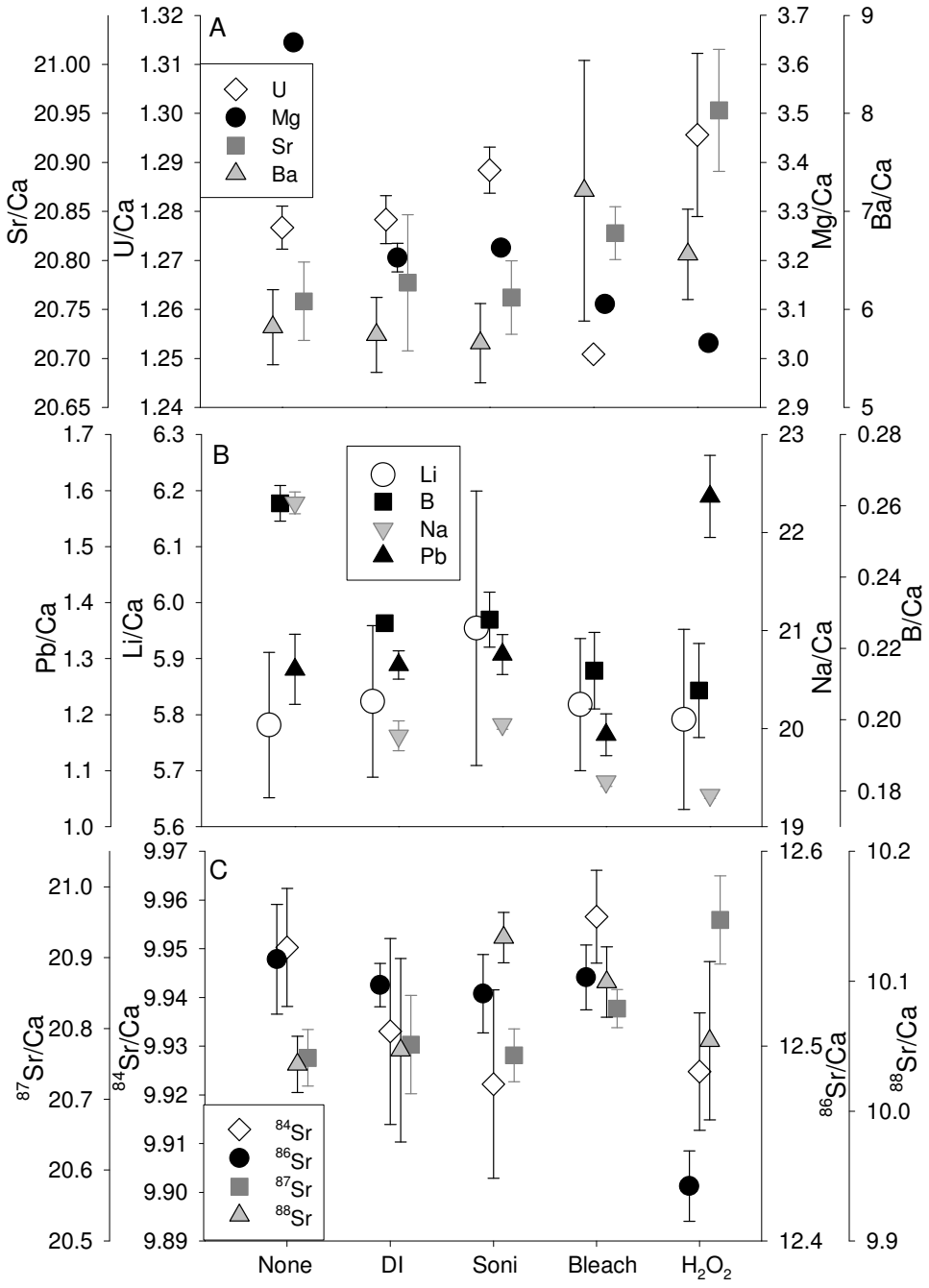
377

378 Figure 3. Element ratios for synthetic aragonite powder (sample 1/19/11 e) prepared with

379 different cleaning protocols. For different Sr isotopes, the Sr/Ca ratio is calculated

380 assuming natural isotopic abundances. Values and symbols are as described for Fig. 2,

381 values for Pb/Ca are μmol/mol.




382

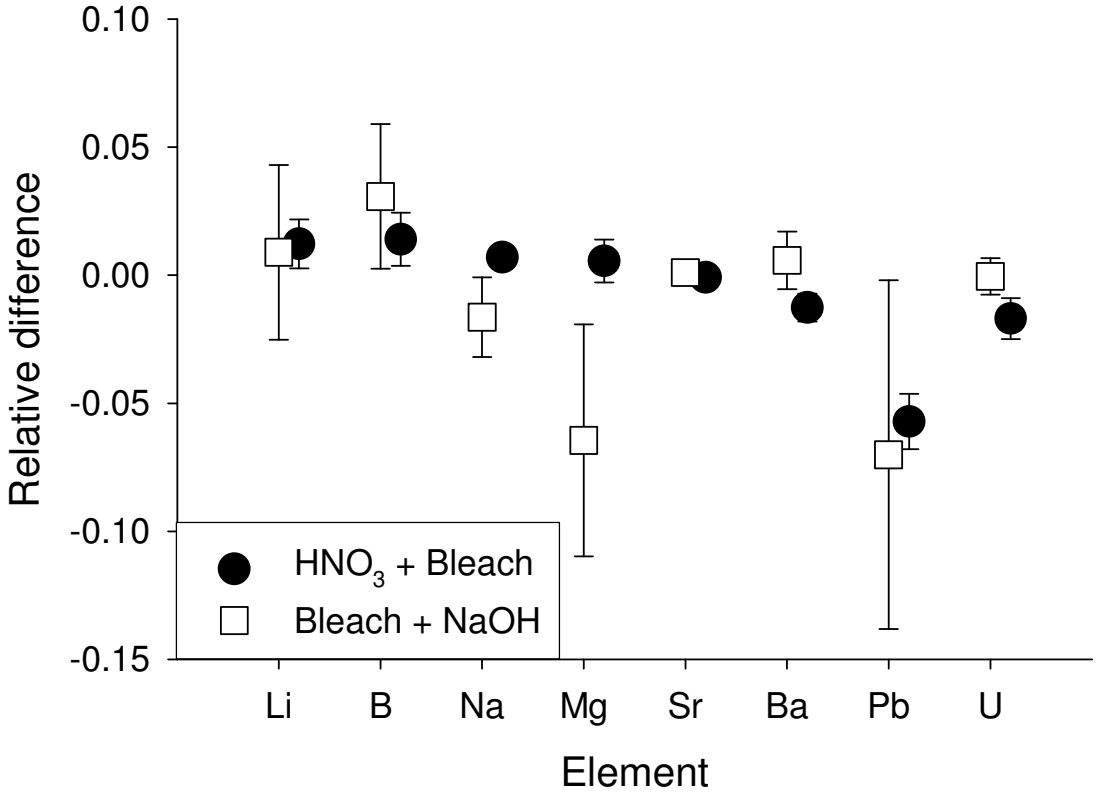
383

384 Figure 4. Element ratios for synthetic aragonite powder (sample 1/19/11 d) prepared with

385 different cleaning protocols. Values are per Fig3.

386 Significant differences were found among cleaning protocols for Mg/Ca ($F_{3,16}$=45.3,
387 p<0.001), Ba/Ca ($F_{3,16}$=30.5, p<0.001), and U/Ca ($F_{3,16}$=28.7, p<0.001) in the *Porites* sp.
388 sample containing organic matter (Fig. S3). Untreated samples had significantly
389 (p<0.005) higher Mg/Ca ratios than samples subject to any of the cleaning procedures
390 and both untreated and rinsed samples had significantly (p<0.005) higher Mg/Ca and
391 Ba/Ca ratios than bleached samples regardless of the bleaching duration. Untreated
392 samples exhibited highly variable U/Ca ratios, although U/Ca tended to be lower in
393 untreated samples than bleached samples. Rinsed samples had significantly (p<0.0001)
394 lower U/Ca ratios than bleached samples. Treating a rinsed sample with concentrated
395 nitric acid increased U/Ca ratios to values (~1.13 μmol/mol) comparable to those
396 measured in bleached samples.
397
398
399 *3.3. Sample loss*
400 Acid washing led to a significant loss of the sample ($F_{2,6}$=29.0, p<.001 for NEP,
401 $F_{2,6}$=82.0, p<0.0001 for synthetic aragonite 1/19/11 e, Fig. 6). For the synthetic aragonite
402 powder treated with $H_2O_2$ (1/19/11 d), the mass was somewhat reduced following
403 treatment ($F_{4,10}$=4.9, p<0.05, $H_2O_2$ lower than untreated p<.05). No significant
404 differences were detected among treatments for foraminifera samples.
405

406




407

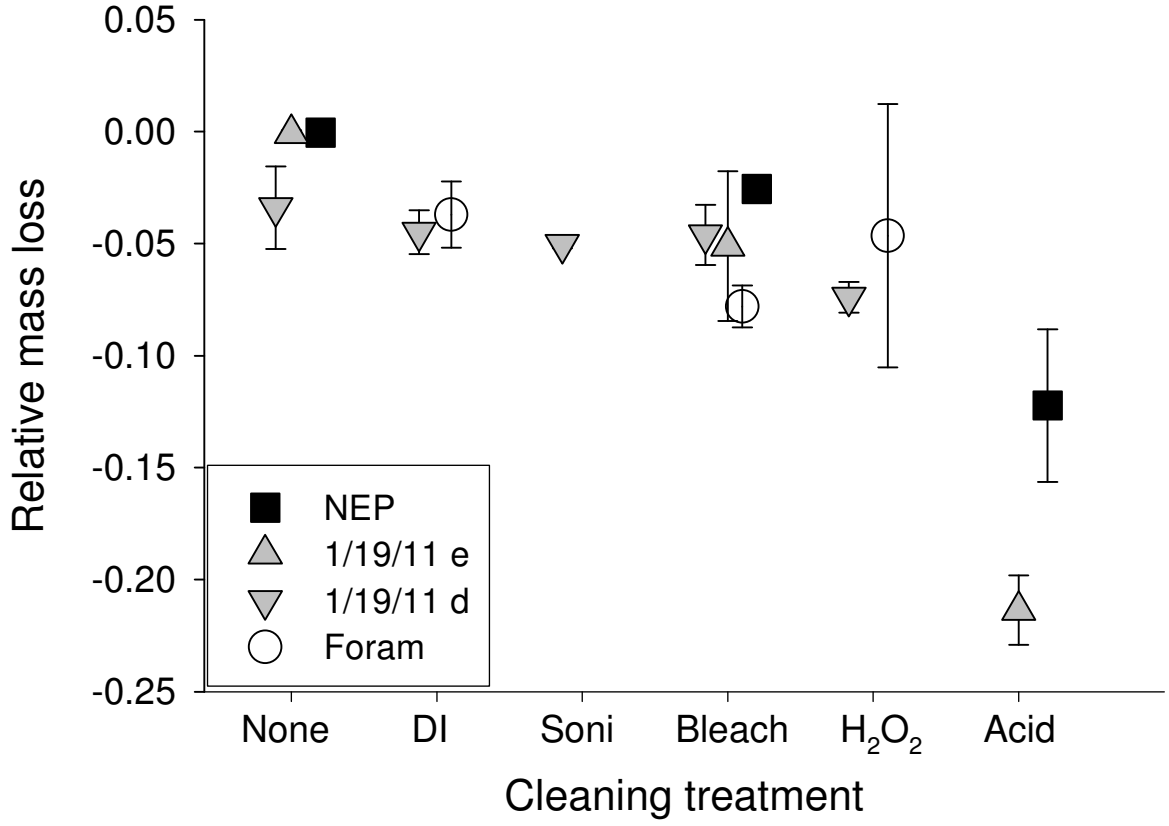
408 Figure 5. Mean relative differences (acid + bleach or bleach + NaOH treated

409 value/bleached value – 1) in M/Ca ratios for different elements measured in various coral

410 samples. Error bars are 2 standard errors.

411

412




413

414 Figure 6. Relative mass loss (mass lost/sample mass) for different sample types (NEP =

415 coral, 1/19/11 e = synthetic aragonite, 1/19/11 d = synthetic aragonite, foram =

416 foraminifera) versus cleaning treatment. Symbols are means, error bars are standard

417 deviation.

418 **4. Discussion**

419

420 *4.1. Boron isotopes*

421 For the majority of samples tested, no significant differences were found in the $\delta^{11}B$
422 values regardless of the cleaning protocol. Only for the synthetic aragonite (1/19/11 e)
423 samples treated with $HNO_3$ was there a significant decline in $\delta^{11}B$ (Fig. 1). Dissolution
424 of synthetic aragonite (1/19/11 e) is expected to decrease $\delta^{11}B$ given the nature of the
425 precipitation experiment. Since aragonite is depleted in $\delta^{11}B$ relative to the solution from
426 which it forms (e.g. Vengosh et al., 1991; Hemming et al., 1995), the solution becomes
427 enriched in $\delta^{11}B$ over the course of precipitation. Moreover, the pH increased toward the
428 end of the experiment (Fig. S1), so $\delta^{11}B$ should increase due to its dependence upon pH
429 (e.g. Klochko et al., 2006). Thus, the final material deposited in the experiment should
430 have the highest $\delta^{11}B$ values. Based on changes in Sr isotopes (discussed below, Fig.
431 S7), we conclude that the material deposited towards the end of the experiment dissolved
432 to the greatest extent during treatment with $HNO_3$.

433 Seawater contamination would be expected to increase $\delta^{11}B$ values due to
434 seawater having a $\delta^{11}B$ of near 40‰. The lack of significant differences between
435 untreated and rinsed samples suggests that seawater contamination did not contribute
436 sufficient boron to affect $\delta^{11}B$ in the samples tested here. However, in some instances
437 sample treatment reduced B/Ca ratios (section 3.2.1). Since no change in $\delta^{11}B$ was
438 detected despite changes in B/Ca, this suggests some of the boron removed had an
439 isotopic composition closer to that of the sample than bulk seawater, such as might be
440 expected for adsorbed borate. Residual organic materials present in the coral and

foraminifera samples did not appear to affect $\delta^{11}B$ values significantly based on the lack of effect of bleach (Fig. 1). For the foraminifera sample, the lack of a significant difference among cleaning treatments may also be due to the relatively low boron concentration in the foraminifera (high Mg-calcite), which is approximately 20% of the concentration measured in a coral (Fig. 2, S2). The relatively low boron concentration led to larger measurement uncertainties, thus limiting our ability to detect any possible effect of cleaning treatments on $\delta^{11}B$ of foraminifera samples.

Visual assessment following sample dissolution suggested bleached powders had less undissolved residue than either rinsed or peroxide treated samples. However residual organic material had no significant effect on boron isotopes suggesting that relatively little boron with a $\delta^{11}B$ composition different from the skeleton was contributed by the organic residue. It should be noted that there are organic materials that do contain boron (e.g. Mohnen 2008), so there may be sample types for which residual organics do influence $\delta^{11}B$, thus it is likely prudent to include an organic removal step as a precautionary measure.

*4.2. Trace elements*

For all aragonite samples, treatment with any of the cleaning procedures led to a significant reduction in Mg/Ca and Na/Ca, and a slight decline in B/Ca (Fig. 2, 3, 4), consistent with seawater, or weakly adsorbed ions of seawater origin, being a contaminating phase. Sample dissolution is unlikely to be responsible for this pattern as little to no sample dissolution was measured for many of the cleaning procedures (Fig. 6). Samples of the $H_2O$ supernatant post rinsing from the synthetic aragonite 1/19/11 d were

464 taken and analyzed for elemental composition. The initial rinses had high Na/Ca and
465 Mg/Ca ratios relative to the bulk precipitate (data not shown), suggesting a seawater or
466 weakly adsorbed component with a composition closer to seawater than that of aragonite,
467 consistent with the patterns measured in the precipitates. Since the synthetic aragonites
468 1/19/11 d and e were spiked with $^{86}Sr$ and $^{87}Sr$ at different time points during their
469 growth, sample dissolution should alter the Sr/Ca ratio differently for different isotopes
470 (Fig. S7). Dissolution of the final precipitate to form would reduce $^{86}Sr$, since this was
471 the final isotope spike added to the experiments. An increase in $^{87}Sr$ would suggest
472 dissolution of the initial material formed (nuclei, which tend to have a higher solubility
473 (e.g. Holcomb et al., 2009)), which precipitated prior to addition of the $^{87}Sr$ spike. In
474 both cases where measurable dissolution of synthetic aragonites 1/19/11 d and e occurred
475 (acid and $H_2O_2$ treatments), $^{86}Sr/Ca$ ratios declined, indicating dissolution of the exterior
476 of the crystals (Fig. S7). Hydrogen peroxide may also attack the site of nucleation, as
477 $^{87}Sr/Ca$ tended to increase following peroxide treatment. This could explain, at least in
478 part, why peroxide treated samples tended to have lower Mg/Ca ratios as well (regions of
479 nucleation tend to be enriched in Mg/Ca relative to the surrounding aragonite crystals
480 (e.g. Holcomb et al., 2009)). Such an explanation contrasts with the findings of
481 Mitsuguchi et al. (2001), who observed that peroxide treatment of coral aragonite resulted
482 in higher Na/Ca and Mg/Ca ratios. However, our observation may be related to particle
483 size as the synthetic aragonites used in our study had, based on microscopy (Fig. S6),
484 particle sizes generally less than 15 μm. The nuclei of the synthetic aragonites were
485 relatively more exposed to the cleaning agents than would be the case with larger particle
486 sizes where nuclei could be protected by surrounding fibers, thus allowing preferential

487 dissolution of the nuclei to occur in the synthetic aragonite. In the work of Mitsuguchi et
488 al. (2001), the typical particle size of crushed coral skeletons was nearly an order of
489 magnitude greater than in our synthetic aragonites. Mitsuguchi et al. (2001) suggested
490 that the large particle size was sufficient to protect centers of calcification from
491 dissolution, and thus lead to enrichment in Na/Ca and Mg/Ca. Acid treatment, however,
492 appears to attack the exterior of the crystal preferentially based on the decline in $^{86}Sr$ not
493 being associated with a significant change in $^{87}Sr$ in the synthetic aragonite. Thus, in a
494 more corrosive solution, faster dissolution of the most exposed regions may dominate,
495 leading primarily to a loss of outer crystal edges. For the coral samples treated with acid
496 prior to bleaching, both particle size (not quantified, but individual particles were visible
497 without magnification) and the use of $HNO_3$ may have contributed to the significant
498 increase in Na/Ca and the trend towards higher Mg/Ca ratios (Fig. 5), consistent with
499 Mitsuguchi et al., (2001). Although particle size represents one potential explanation for
500 differences in patterns between synthetic and biogenic samples, there could also be other
501 differences (e.g. organic compounds) between these samples which contributed to the
502 observed patterns.
503
504 Pb/Ca and U/Ca ratios showed similar patterns, tending to be enriched when dissolution
505 occurred, and reduced by treatment with bleach (Figs. 2,3,4). Although the reasons for
506 this behavior are unknown, it may in-part reflect surface adsorption of Pb and U (Fabry
507 and Delaney, 1989; Hong et al., 2002; Godelitsas et al., 2003; Rouff et al., 2005; Du et
508 al., 2011). An enrichment of Pb and U on either the crystal or tube surface may result
509 from exposure to mildly acidic conditions due to sample dissolution releasing U and Pb

510 from the aragonite - which in-turn may preferentially adsorb onto surfaces, thus leading
511 to enrichment in the remaining sample. Complexation of Pb and U (Turner et al., 1981;
512 Millero et al., 2009) in the bleach solution may help remove ions adsorbed to surfaces.
513 Any enrichment due to acid leaching can potentially be removed by subsequent
514 bleaching, and the combination of acid leaching and bleaching may be more effective
515 than bleach alone at removing any surface enrichment (Fig. 5). However, bleach does
516 not always reduce U/Ca, nor does NaOH (Figs. S4,S5), suggesting that it is neither
517 NaOCl nor high pH that is primarily responsible for removing adsorbed U and Pb.
518 Carbonate ($CO_3^{2-}$) is known to complex both U and Pb (Turner et al., 1981; Millero et al.,
519 2009) and $CO_3^{2-}$ has been used to remove adsorbed U in other studies (Galun et al.,
520 1983). Carbonate concentrations in the bleach or NaOH solution likely increase over
521 time due to a gradual uptake of atmospheric $CO_2$ by the solution which converts to $CO_3^{2-}$
522 under the high pH conditions of the bleach or NaOH solutions. Variations in the $CO_3^{2-}$
523 concentration of the cleaning solution could thus contribute variability to the change in
524 U/Ca due to bleaching (Figs. S4,S5).
525
526 *4.3. Organic materials*
527 Although bleaching reduced Ba/Ca ratios in the organic rich coral sample, and longer
528 bleaching treatments resulted in more consistent reductions than shorter treatments (Fig.
529 S3), Ba/Ca remained higher than would generally be expected. This is consistent with
530 other studies which report anomalously high Ba/Ca ratios within the tissue layer of coral
531 cores (e.g. Tudhope et al., 1996; Sinclair et al., 1998; Alibert et al., 2003; Fallon et al.,
532 2003). A wide range of cleaning approaches has been tested to reduce Ba/Ca, however

Ba/Ca ratios generally remain elevated despite cleaning (e.g. Tudhope et al., 1996; Sinclair, 2005). Our observations are consistent with either organic bound Ba (Flor and Moore, 1977; Lea and Boyle, 1993; Reichelte and McOrist, 2003) or a Ba containing phase soluble at high pH (Nagtegaal et al., 2012) making a substantial contribution to the Ba enrichment as bleach greatly reduced the Ba/Ca ratio. However whether the remaining enrichment is due to refractory organic materials or other factors is not known.

The increase in U/Ca following bleaching in organic rich coral samples (Fig. S3) likely reflects adsorption of U by the insoluble organic materials present in the unbleached samples. Though not significant, a similar trend was observed for the foraminifera sample, with both bleach and peroxide treatments being associated with higher U/Ca. Uranium is known to adsorb onto a wide range of organic materials (Amiel et al., 1973b; Galun et al., 1983; Semiao et al., 2010), thus oxidation of those organic materials prior to sample dissolution should increase the concentration of U free in solution. When the organic materials were not oxidized prior to dissolution but rather were oxidized with hot nitric acid post-dissolution, U/Ca ratios were similar (1.13 μmol/mol) to those measured in bleached samples (Fig. S3). This suggests adsorption of U by organics as a reason low U/Ca ratios were obtained in samples not treated with an organic oxidation step. For the coral sample used here bleach appears to be sufficient to remove the bulk of the organic material capable of binding U, however for some coral samples bleach alone appears to be insufficient and additional oxidative steps are required to obtain U/Ca values near the range of reported values (data not shown).

556 *4.4. Cleaning recommendations*

557 *4.4.1. Rinsing and initial organic removal steps*

558 Our results confirm the findings of Mitsuguchi et al. (2001) and Watanabe et al. (2001)
559 that sample cleaning treatments help to remove contaminants likely of seawater origin
560 (Mg, Na). Further treatment with bleach reduces the amount of organic material visible
561 in the sample without significant sample dissolution and appears more effective in
562 removing organic materials than $H_2O_2$ (using similar incubation durations) consistent
563 with many prior comparisons (Pingitore et al., 1993; Gaffey and Bronnimann, 1993;
564 Krause-Nehring et al., 2011; Nagtegaal et al., 2012), though not all (e.g. Pak et al., 2004).
565 For any sample treatment procedure, rinsing with $H_2O$ is a useful first step as it helps to
566 remove residual seawater which might otherwise contribute ions which could form
567 precipitates during subsequent cleaning steps (e.g. section 3.2.2).
568 Although samples can be rinsed briefly without measureable sample loss (Fig. 6), care
569 should still be taken to avoid excessive exposure to water as both dissolution and
570 recrystallization can occur with prolonged exposure (Amiel et al., 1973a,b; Yoshioka et
571 al., 1986; Pingitore et al., 1993; Holcomb et al., 2009, Shirai et al., 2012). In some
572 instances the pH of the water used for rinsing has been elevated in an effort to reduce
573 dissolution (e.g. Bairbakhish et al., 1999; Blanco-Ameijeiras et al., 2012; Heinmann et
574 al., 2012), however, the effectiveness of this procedure is unknown. The use of sodium
575 hydroxide solutions (~5 M), though effective in reducing dissolution, has been associated
576 with recrystallization (Pingitore et al., 1993; Krause-Nehring et al., 2011), and basic
577 detergent solutions have been found to enhance dissolution (Pingitore et al., 1993), thus
578 elevated pH does not necessarily prevent alteration of the sample during rinsing. It

579 should be noted that although strong NaOH solutions have been shown to affect samples,
580 much less work has been conducted on how less concentrated bases influence sample
581 composition (Table S1), so weakly basic solutions may satisfactorily reduce dissolution.
582 Treatment with acidic solutions (unbuffered $H_2O_2$ or $HNO_3$) can lead to significant
583 dissolution (Pingitore et al., 1993) and alter the composition of heterogeneous samples
584 (Figs. 3,4,6), though there are instances in which some dissolution is considered desirable
585 (e.g. Boiseau and Juillet-Leclerc, 1997). The use of bleach in place of acidic reagents
586 appears advisable for preserving the sample, however for some isotopic ratios ($\delta^{13}C$,
587 $\delta^{18}O$) bleach may affect values (Grottoli et al., 2005; Wierzbowski, 2007). Other
588 approaches using non-acidic reagents such as buffered $H_2O_2$ may also provide
589 satisfactory results (e.g. Stoll et al., 2001; Blanco-Ameijeiras et al., 2012). Any cleaning
590 agent should be used with caution as the presence/concentrations of various ions can
591 dramatically affect the rate of ion exchange, dissolution, and recrystallization (Amiel et
592 al., 1973a,b; Yoshioka et al., 1986; Pingitore et al., 1993).
593
594 *4.4.2. Removing refractory organics*
595 For samples containing refractory organic matter not removed with initial bleach
596 or peroxide treatments an additional oxidation step post-dissolution may be needed for
597 determination of elements such as U. Incubation in hot nitric acid appears to
598 oxidize/hydrolyze sufficient organic material to improve U/Ca values; however this
599 approach was not extensively tested and may not be sufficient for obtaining reliable U/Ca
600 ratios from different sample types. For samples containing refractory organic materials it
601 would be worth testing some of the established oxidation techniques, such as: photo-

602 oxidation (Spivack and Edmond, 1986; Wara et al., 2003), peroxide treatment (Amiel et
603 al., 1973a; Ihlenfeld et al., 2003), perchloric acid (Tatsumoto and Goldberg, 1959),
604 ashing combined with concentrated $HNO_3$ and evaporation (Robinson et al., 2004), or
605 concentrated $HNO_3$ and $H_2O_2$ (Bohm et al., 2006).
606
607 *4.4.3. Removing adsorbed species*
608 For measurements of species which may adsorb to surfaces (such as Pb and U), we have
609 shown that bleaching can help to remove adsorbed Pb and U, possibly due to carbonate
610 present in the solution. Although carbonate solutions may be useful for removing
611 adsorbed U or Pb species (Galun et al., 1983), there are a number of established protocols
612 for removing these species. Acetate buffers can reduce adsorbed U and have been used
613 for this purpose (Amiel et al., 1973b; Wang et al., 2013b). For Pb and trace metals, short
614 (<2 min) acid wash steps have also been shown to be effective in removing surface
615 contaminants, but longer exposure leads to re-enrichment as the pH of the acid wash
616 solution rises (Shen and Boyle, 1988). As an alternative to extensive sample cleaning
617 procedures, flow through dissolution systems have also been developed for measuring
618 species which tend to adsorb to surfaces (e.g. Klinkhammer et al., 2004).
619
620
621 *5. Conclusions*
622 For the samples tested, $\delta^{11}B$ appears to be relatively insensitive to sample cleaning
623 methods, with significant changes occurring only for compositionally heterogeneous
624 samples subjected to dissolution. However other trace elements were more strongly

625 affected by cleaning. Rinsing samples with $H_2O$ and treatment with NaOCl (bleach)
626 appeared to cause little dissolution. Rinsing helps to remove seawater contamination
627 and/or surface adsorbed Na and Mg, while bleach or $H_2O_2$ solubilize much of the organic
628 material. These cleaning agents may thus be useful for removing such contaminants from
629 $CaCO_3$ samples.
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647

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951 **Supplemental materials**

952

953 *Synthetic aragonite*

954 Alkalinity and pH samples were taken periodically over the course of the aragonite
955 growth experiments. Alkalinity samples were diluted immediately with a ~0.68 M NaCl
956 solution. Measurements were made as described by Holcomb et al. (2012). Alkalinity,
957 pH, predicted quantities of aragonite precipitated, and the times of isotope spikes are
958 plotted in Figure S1. A scanning electron microscopy (SEM) image of the resultant
959 precipitate is shown in Figure S6.

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961

962 *Supplemental results and discussion*

963 In treatments of the TS3 aragonite powder conducted at UWA, no significant differences
964 were found among rinsing, bleaching, and NaOH for any of the measured ratios other
965 than U/Ca ($F_{2,6}$ = 14.4, $p<0.01$). Bleached samples had higher U/Ca than rinsed ($p<0.01$)
966 and NaOH ($p<0.05$) treated samples (Fig. S4). For the same sample treated at WHOI,
967 there was no significant effect of NaOH concentration between 0.006 M and 0.1 M on
968 Mg/Ca, Sr/Ca, Ba/Ca, or U/Ca. However, bleach significantly increased Sr/Ca
969 ($F_{4,17}$=43.1, bleach higher than other treatments $p <0.001$) and decreased U/Ca
970 ($F_{4,17}$=32.3, bleach lower than other treatments $p <0.001$) relative to cleaning with $H_2O$ or
971 any of the NaOH treatments. (Figure S5).

972

Although both bleach (Figs. 2,3,4,S5) and NaOH (see results, section 3.2.2) were associated with declines in the U/Ca ratio, this was not always observed (Fig. S4), even in treatments of the same sample (Figs. S4,S5). This suggests that the reduction in U/Ca is not related to the high pH of the wash solution alone, but due to some other factor. Variation in the $CO_3^{2-}$ content of the solution (due to variable uptake of $CO_2$) is suggested as a potential explanation (see discussion section 4.2).

In one instance, treatment with bleach was associated with an unexpected increase in Sr/Ca (Fig. S5). Although it is not known why bleach might result in an increase in Sr/Ca, it could be related to Sr present in the bleach solution used. Krause-Nehring et al. (2011) measured the composition of the bleach solution used in their experiments and found high Sr/Ca ratios (as well as contamination with other elements), suggesting that bleach has the potential to contaminate samples. Nagtegaal et al., (2012) also reported differing effects of bleach obtained from different suppliers. Hydrogen peroxide too has the potential to contaminate samples. For a synthetic aragonite sample (1/19/11 d), treatment with $H_2O_2$ was associated with an increase in Sn/Ca, which persisted despite repeated rinsing with $H_2O$ post treatment (data not shown). Thus care must be taken in selecting reagents for cleaning samples to avoid introducing new sources of contamination.

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1154

**Supplemental tables and figures**

Table S1. Studies examining the effects of different cleaning procedures on calcium carbonate samples. Independent treatments that were compared are separated by ",", mixed reagents are indicated by "/" between reagent names. For studies which compared multi-step procedures instead of individual treatments, major steps are listed with "+" between each step. Only the major treatment compared is listed in the cleaning agents column, some studies used an initial pre-treatment prior to comparing specific reagents. Studies are ordered from most recent to earliest.

| Cleaning agents | Sample type | Measurements | Study |
|---|---|---|---|
| rinsing, $H_2O_2$, $HNO_3$, NaOH, NaOCl | abiotic and coral aragonite, foraminifera calcite | $\delta^{11}B$, Li, B, Na, Mg, Sr, Ba, Pb, U | current study |
| $H_2O_2$/NaOH + $HNO_3$ + hydrazine/ammonia/citrate | abiotic calcite | B | Uchikawa et al., 2015 |
| NaOCl, persulfate | coral aragonite | $\delta^{15}N$ | Wang et al., 2015 |
| rinsing and methanol, $H_2O_2$/NaOH, hydrazine/ammonia/citrate | ostracod calcite | Mg, Al, Mn, Fe, Sr, microscopy | Gray et al., 2014 |
| $H_2O_2$/NaOH, $HNO_3$, hydrazine/ammonia/acetate, combinations thereof | foraminifera calcite | B | Misra et al., 2014a |
| $H_2O_2$/NaOH, $HNO_3$, hydrazine/ammonia/acetate, combinations thereof | foraminifera calcite | $\delta^{11}B$ | Misra et al., 2014b |
| $H_2O_2$, $H_2O_2$/$(NaPO_3)_6$, $Na_4P_2O_7$ | foraminifera calcite sediments | pH, fragmentation, $\delta^{13}C$, $\delta^{18}O$, Mg | Feldmeijer et al., 2013 |
| rinsing, $H_2O_2$/NaOH, NaOCl, heat, combinations thereof | sea urchin calcite | Mg, Sr | LaVigne et al., 2013 |
| $H_2O_2$/NaOH, $HNO_3$, hydrazine/ammonia/citrate | foraminifera calcite | Mg, Al, Mn, Zn, Sr, Ba | Marr et al., 2013 |
| NaOCl, heat + NaOCl | brachiopod | $\delta^{11}B$ | Penman et al., |

| | | | |
|---|---|---|---|
| | calcite | | 2013 |
| methanol, acetate | coral aragonite | $\delta^{25}Mg$, $\delta^{26}Mg$ | Saenger et al., 2013 |
| $H_2O_2$/NaOH + hydrazine/ammonia/citrate + DTPA/NaOH | foraminifera calcite | Mg, Ba | Vetter et al., 2013 |
| rinsing, methanol, acetate | abiotic aragonite | $\delta^{26}Mg$, Mg, Sr, Ba, U | Wang et al., 2013b |
| rinsing, $H_2O_2$/NaOH, NaOCl, $NH_2OH{\cdot}HCl/NH_4OH$ | abiotic and coccolith calcite, organics | Mg, P, Ca, Fe, Sr | Blanco-Ameijeiras et al., 2012 |
| $H_2O_2$/NaOH, $HNO_3$, hydrazine/ammonia/citrate, combinations thereof | foraminifera calcite | U | Boiteau et al., 2012 |
| $H_2O$ + methanol + $H_2O_2$/NaOH + $HNO_3$ | foraminifera calcite | Mg, S, Ca, Mn, Fe | Glock et al., 2012 |
| rinsing, $H_2O_2$, $HNO_3$ | coral aragonite | Na, Mg, K, Sr | Mitsuguchi and Kawakami, 2012 |
| $H_2O_2$, $HNO_3$, NaOCl | coral aragonite (slabs) | $\delta^{13}C$, $\delta^{18}O$, Mg, Sr, Y, Ba, U, luminescence | Nagtegaal et al., 2012 |
| rinsing, $H_2O_2$/NaOH, hydrazine/ammonia/citrate, DTPA/NaOH | foraminifera calcite | Nd | Roberts et al., 2012 |
| $H_2O_2$ | coral aragonite | $\delta^{13}C$, $\delta^{18}O$, $\Delta_{47}$ | Saenger et al., 2012 |
| rinsing, $H_2O_2$, NaOCl, NaCl | fossil calcium carbonates | $\delta^{34}S$, S | Wotte et al., 2012 |
| rinsing, $H_2O_2$, $HNO_3$ | otolith aragonite | Mg, Mn, Sr, Ba | Davies et al., 2011 |
| rinsing, $H_2O_2$, NaOH, NaOCl, acetone | bivalve aragonite, abiotic calcite | N, Mg, Ca, Mn, Sr, Ba, crystallography | Krause-Nehring et al., 2011 |
| citrate, hydrazine, $NH_4OH$, and mixtures thereof | foraminifera calcite | Na, Mg, Al, Mn, Fe, Sr, Cd, Ba, La, Ce, Nd, U | Bian and Martin, 2010 |
| physical cleaning, $H_2O_2$/NaOH + $H_2O_2$/ $HClO_4$, methanol + $HNO_3$, hydrazine/ammonia/citrate, EDTA + $HNO_3$ | coral aragonite | Nd isotopes, Nd, Th, U | van de Flierdt et al., 2010 |
| rinsing, $H_2O_2$, | foraminifera | pH, $\delta^{13}C$, $\delta^{18}O$, | Fallet et al., 2009 |

| | | | |
|---|---|---|---|
| $H_2O_2$/NaOH, heat | calcite and bivalve aragonite sediments | Mg, Fe, Sr, Ba | |
| rinsing, $H_2O_2$/NaOH, $HNO_3$ | coral aragonite | Cu, Sn | Inoue et al., 2009 |
| rinsing/$H_2O_2$/$HNO_3$ | otolith aragonite | Al, V, Mn, Co, Ni, Cu, Zn, Ga, Cd, Pb, Bi | Arslan and Secor 2008 |
| rinsing, ethanol (effect of evaporation) | ostracod calcite | $\delta^{13}C$, $\delta^{18}O$, microscopy | Mischke et al., 2008 |
| $H_2O_2$, NaOCl, heat, ethanol, methanol, sonication, + combinations thereof | foraminifera calcite | $\delta^{13}C$, $\delta^{18}O$ | Serrano et al., 2008 |
| rinsing + methanol, $H_2O_2$, methanol | ostracod calcite | $\delta^{13}C$, $\delta^{18}O$ | Li et al., 2007 |
| $H_2O_2$, NaOCl, heat | abiotic and biotic calcite and aragonite, organics | $\delta^{13}C$, $\delta^{18}O$ | Wierzbowski, 2007 |
| rinsing, $H_2O_2$/NaOH, NaOH, $NH_3$, hydrazine, citrate, and mixtures thereof | foraminifera calcite | Li, B, Mg, Mn, Zn, Sr, Cd, U | Yu et al., 2007 |
| rinsing, $H_2O_2$/NaOH, $NH_2OH{\cdot}HCl$ /$NH_3$, $Na_2S_2O_4$/citric acid, methanol | ostracod calcite | Mg, Sr | Jin et al., 2006 |
| $H_2O_2$, NaOCl, heat, $NH_2OH{\cdot}HCl$ /$NH_3$, $Na_2S_2O_4$/citric acid | ostracod calcite | $\delta^{13}C$, $\delta^{18}O$, Mg, Sr | Keatings et al., 2006 |
| hydrazine/ammonia/citrate | foraminifera calcite | Mg, Mn, Fe, Sr | Weldeab et al., 2006 |
| rinsing, $H_2O_2$, NaOCl | coral aragonite | $\delta^{13}C$, $\delta^{18}O$ | Grottoli et al., 2005 |
| rinsing, $H_2O_2$/NaOH, $HNO_3$, methanol, hydrazine/ammonia/citrate, | foraminifera calcite | Mg, Al, Mn, Sr | Pena et al., 2005 |
| $H_2O_2$ | foraminifera calcite | $\delta^{18}O$ | Waelbroeck et al., 2005 |
| rinsing, $H_2O_2$/NaOH, $HNO_3$ | coral aragonite | Cu, Sn | Inoue et al., 2004a |
| $HNO_3$, ethanol, $H_2O_2$/NaOH/hydrazine/am | foraminifera calcite | Mg | Klinkhammer et al., 2004 |

| | | | |
|---|---|---|---|
| monia/citrate | | | |
| rinsing, $H_2O_2$/NaOH, NaOCl | foraminifera calcite | Mg, Mn, Cd, Sr, Ba, U | Pak et al., 2004 |
| rinsing, $H_2O_2$/NaOH, $HNO_3$, hydrazine/ammonia/citrate | foraminifera calcite | Mg, Mn, Fe, Sr | Barker et al., 2003 |
| $H_2O$, $H_2O_2$, NaOH, NaOCl | coral aragonite | microscopy | Clode and Marshall, 2003 |
| rinsing ($H_2O$ + methanol)/$HNO_3$, $H_2O_2$/NaOH, hydrazine/ammonia/citrate, DTPA/NaOH | foraminifera calcite | Mg, Sr | Martin and Lea, 2002 |
| rinsing, $H_2O_2$, $HNO_3$ | coral aragonite | Na, Mg, Sr | Mitsuguchi et al., 2001 |
| rinsing, $H_2O_2$/NaOH, $H_2O_2$/NaOCl, TMAH/$H_2O$, TMAH/ethanol, natural oxidation | abiotic and coccolith calcite, organics | Mg | Stoll et al., 2001 |
| rinsing, $H_2O_2$, $H_2O_2$/NaOH, $HNO_3$, NaOH, NaOCl | coral aragonite | $\delta^{13}C$, $\delta^{18}O$, Mg, Sr | Watanabe et al., 2001 |
| rinsing, $HNO_3$, combinations thereof | otolith aragonite | Li, Mg, Zn, Sr, Ba | Campana et al., 2000 |
| rinsing, $H_2O_2$/NaOH, $HNO_3$, hydrazine/ammonia/citrate | foraminifera calcite | Mg | Hastings et al., 1998 |
| $H_2O_2$, heat | coral aragonite | $\delta^{13}C$, $\delta^{18}O$ | Boiseau and Juillet-Leclerc, 1997 |
| $H_2O_2$/$(NaPO_3)_n$, $HNO_3$, NaOCl | coral aragonite | organic carbon | Hart et al., 1997 |
| treatment order for: hydrazine/ammonia/citrate + $H_2O_2$/NaOH | foraminifera calcite | Cd | Rosenthal et al., 1997 |
| $H_2O_2$/NaOH, hydrazine/ammonia/citrate | Halimeda aragonite | Mg, Mn, Sr, Cd | Delaney et al., 1996 |
| $H_2O_2$, heat | mollusc shell powders | $CO_2$, Na, Mg, $SO_4$, Cl, Ca, Sr, crystallography | Lecuyer, 1996 |
| rinsing, $H_2O_2$/NaOH, $HNO_3$, hydrazine/ammonia/citrate | coral aragonite | U | Shen and Dunbar, 1995 |
| $H_2O_2$, $H_2O_2$/NaOH, NaOH, NaOCl | biotic calcite and aragonite | N, C, microscopy, water, organics | Gaffey and Bronnimann, 1993 |

| | | | |
|---|---|---|---|
| DTPA, hydrazine/ammonia/citrate | foraminifera calcite, coral aragonite | Ba | Lea and Boyle, 1993 |
| $H_2O$, $H_2O_2$, NaOH, NaOCl, ethanol, acetone, detergent | abiotic calcite and aragonite | Ca release, crystallography | Pingitore et al., 1993 |
| rinsing, $NH_2OH{\cdot}HCl$ /$NH_3$, $Na_2S_2O_4$/citric acid | ostracod calcite | Mg, Ca, Mn, Fe, Sr | Holmes, 1992 |
| heat (various temperatures) | biogenic carbonates (various species) | Mg, S, Ca, Sr, microscopy, crystallography, water content, hydrogen bonding, hydroxide, organics, S oxidation state | Gaffey et al., 1991 |
| NaCl, $NaHCO_3$, $Na_2CO_3$, $(NaPO_3)_n$, $Na_5P_3O_{10}$ | ostracod calcite | microscopy | Kontrovitz et al., 1991 |
| $H_2O_2$, NaOH, NaOCl, heat | abiotic aragonite | Na, Mg, K, Ca, Mn, Fe, Sr | Love and Woronow, 1991 |
| rinsing, $H_2O_2$/NaOH, $HNO_3$, hydrazine/ammonia/citrate | coral aragonite | Mn | Shen et al., 1991 |
| $H_2O_2$/NaOH, $HNO_3$, hydrazine | coral aragonite | Cu | Linn et al., 1990 |
| $H_2O_2$/methonal/heat with/without sonication | foraminifera calcite, marble, organics | $\delta^{13}C$, $\delta^{18}O$ | Sarkar et al., 1990 |
| $H_2O_2$/NaOH, heat, grinding | pteropod and heteropod aragonite | Pb, Po | Fabry and Delaney, 1989 |
| $H_2O_2$, heat | coral aragonite | $\delta^{13}C$, $\delta^{18}O$ | McConnaughey, 1989 |
| rinsing, $H_2O_2$/NaOH, $HNO_3$, hydrazine/ammonia/citrate | coral aragonite | Zn, Cd, Pb | Shen and Boyle, 1988 |
| NaOCl, heat | pteropod aragonite | $\delta^{13}C$, $\delta^{18}O$ | Grossman et al., 1986 |
| acetate, $NH_2OH{\cdot}HCl$ /$NH_3$, $Na_2S_2O_4$/citric acid, $CO_2$ | foraminifera calcite | Mg, Al, Ca, Mn, Fe, Ni, Cu, Zn, Cd | Boyle, 1981 |
| heat | foraminifera | $\delta^{13}C$, $\delta^{18}O$ | Erez and Honjo, |

| | | | |
|---|---|---|---|
| | calcite | | 1981 |
| $H_2O_2/NH_3$, heat | foraminifera calcite | $\delta^{13}C$ | Ganssen 1981 |
| NaOCl | ostracod calcite | $\delta^{13}C$, $\delta^{18}O$ | Durazzi, 1977 |
| NaOCl, heat | coral aragonite | $\delta^{13}C$, $\delta^{18}O$ | Land et al., 1975 |
| heat | bivalve and abiotic $CaCO_3$ | $\delta^{13}C$, $\delta^{18}O$ | Mook, 1971 |
| NaOCl | foraminifera calcite | $\delta^{13}C$, $\delta^{18}O$ | Duplessy et al., 1970 |
| NaOCl, heat | biotic and abiotic $CaCO_3$ | $\delta^{18}O$ | Emiliani, 1966 |

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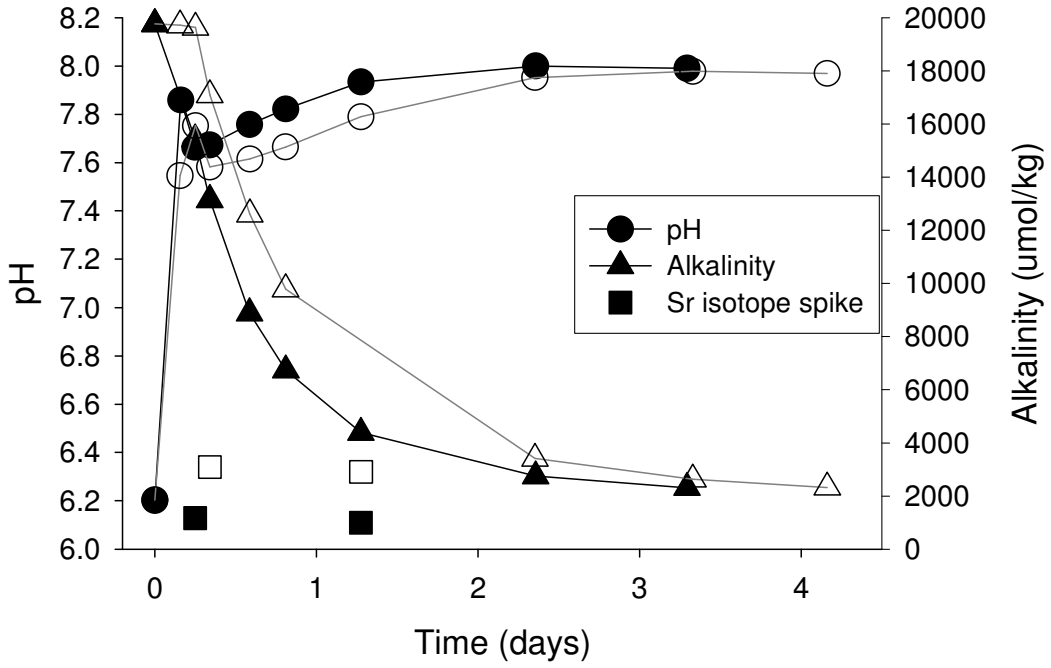
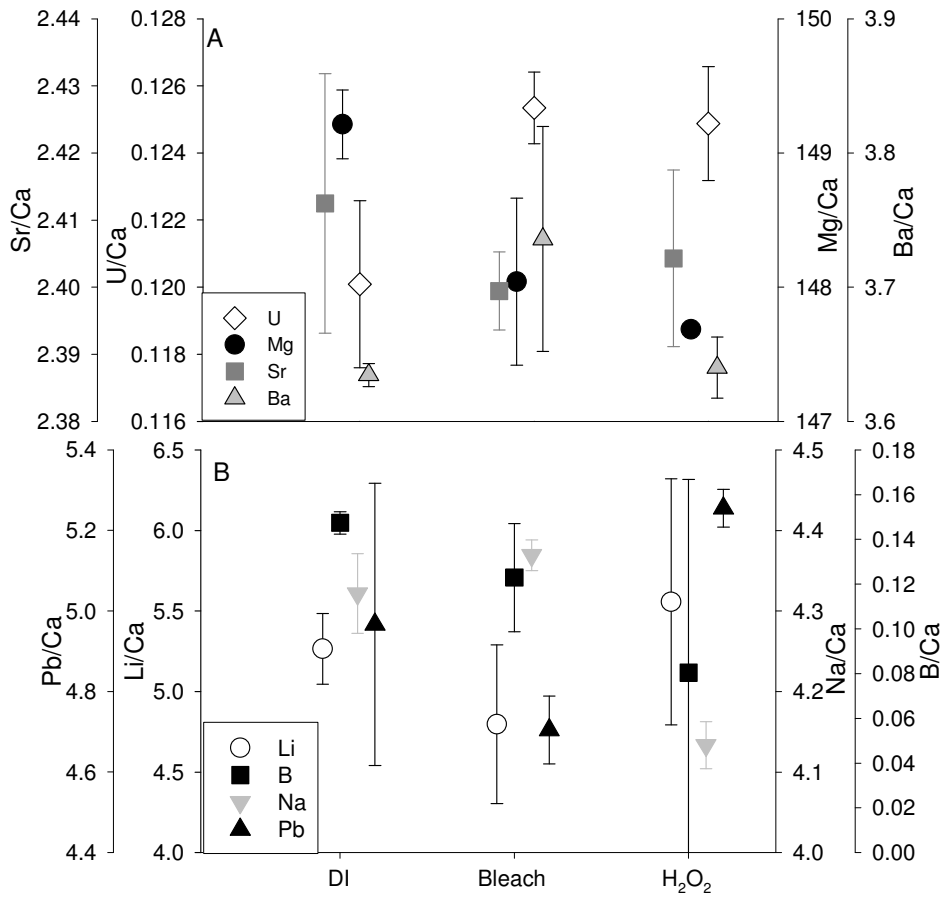



Figure S1. Solution chemistry ($pH_T$, alkalinity) during growth of synthetic aragonites. In both experiments the $^{87}Sr$ isotope spike was added first, $^{86}Sr$ second. Experiment 1/19/11 e is shown in open symbols, 1/19/11 d in filled. Symbols represent individual measurements.




1173

1174 Figure S2. Element ratios for a foraminifera sample prepared with different cleaning

1175 protocols. Values are mmol Sr, Mg, Na, and B, or µmol Pb, U, Ba, and Li per mol Ca;

1176 symbols are means, error bars are 2 standard errors.

1177

1178

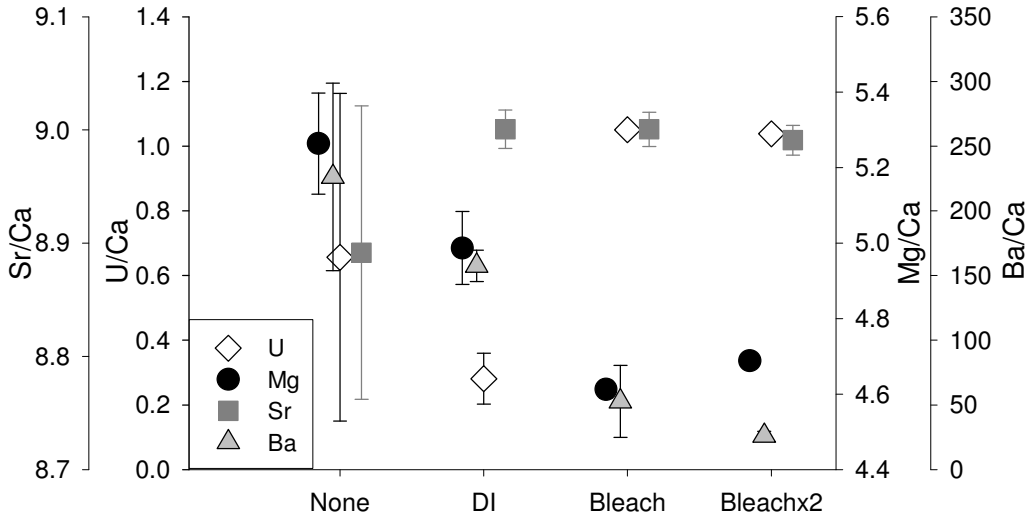
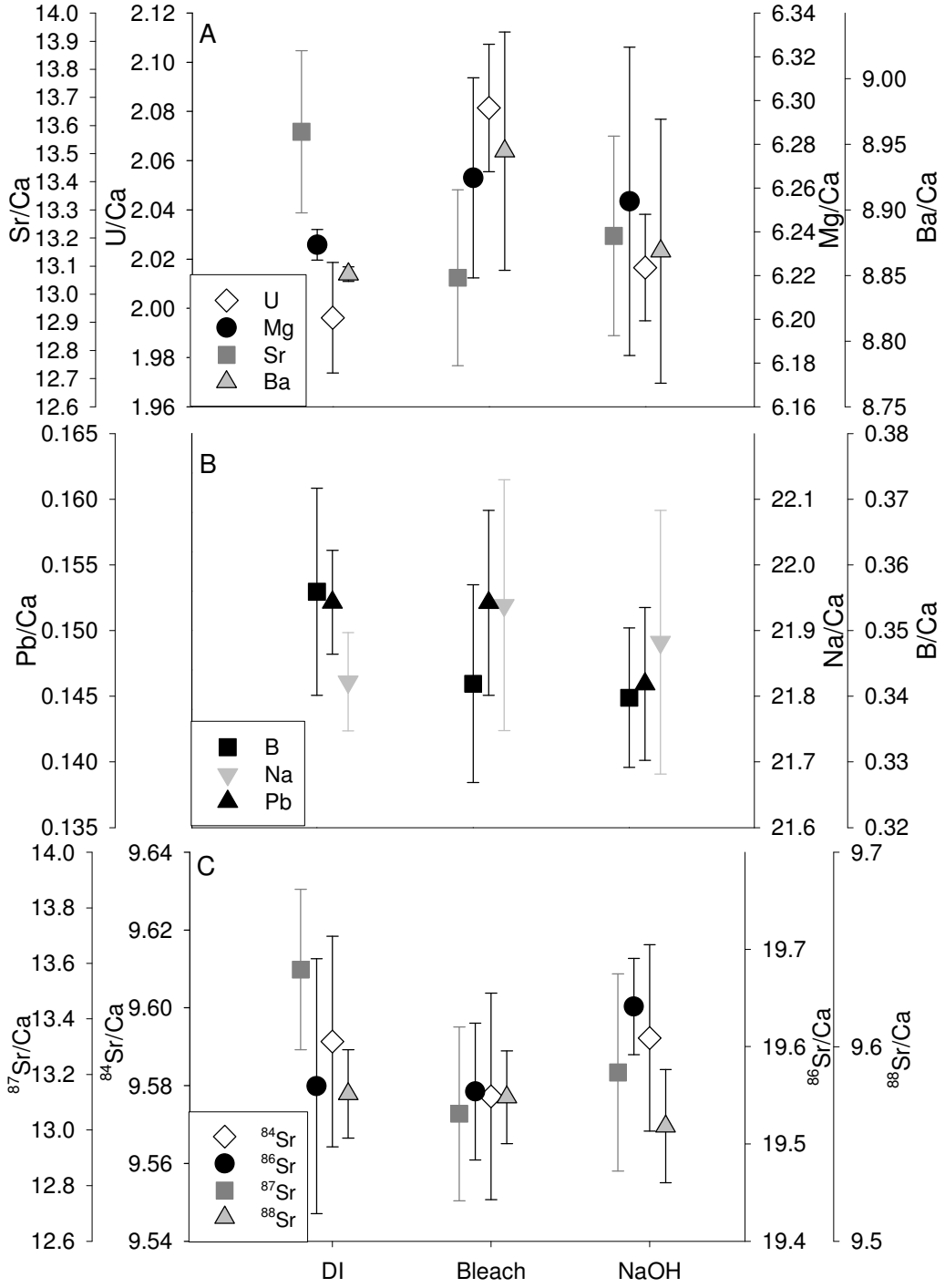



Figure S3. Element ratios for a *Porites sp.* sample containing tissue prepared with different cleaning protocols. The intensive bleaching procedure is represented by bleachx2. Values are mmol Sr, Mg, or μmol U and Ba per mol Ca; symbols are means, error bars are 2 standard errors.

1185


A
B
C
Sr/Ca
U/Ca
Mg/Ca
Ba/Ca
Pb/Ca
Na/Ca
B/Ca
$^{87}$Sr/Ca
$^{84}$Sr/Ca
$^{86}$Sr/Ca
$^{88}$Sr/Ca
U
Mg
Sr
Ba
B
Na
Pb
$^{84}$Sr
$^{86}$Sr
$^{87}$Sr
$^{88}$Sr
DI
Bleach
NaOH

1186

Figure S4. Element ratios for a synthetic aragonite sample (TS3) prepared with different cleaning protocols (done at UWA). Values are mmol Sr, Mg, Na, and B, or µmol Pb, U, and Ba per mol Ca; symbols are means, error bars are 2 standard errors.

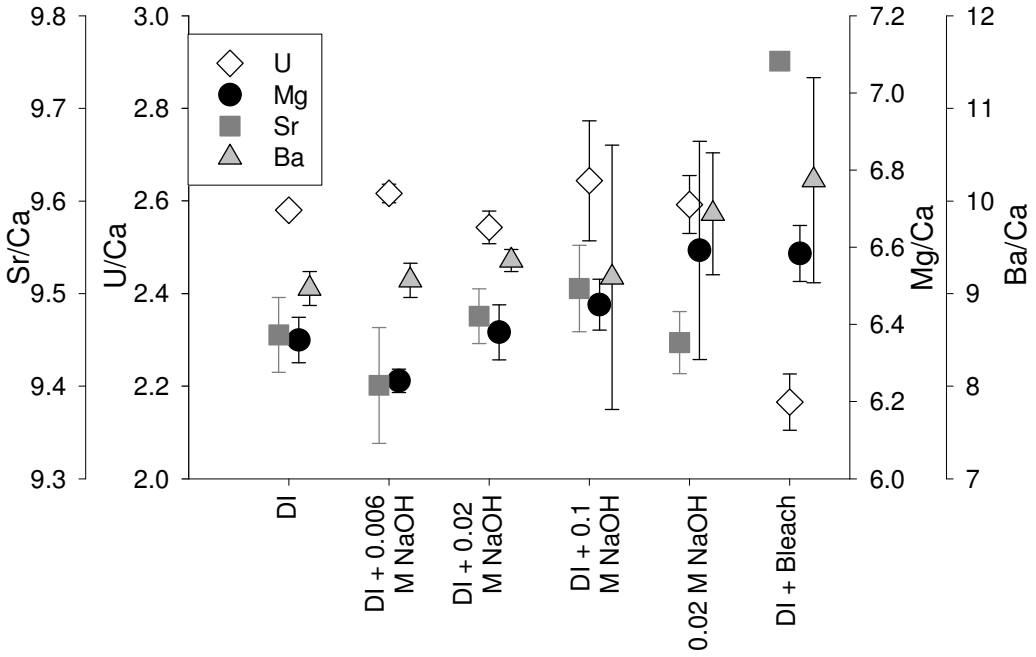



Figure S5. Element ratios for a synthetic aragonite sample (TS3) prepared with different cleaning protocols (done at WHOI). Cleaning protocols consist of water rinses (DI) and basic cleaning solutions (NaOH or NaOCl) used in different combinations and concentrations. Values are mmol Sr, Mg, or µmol U and Ba per mol Ca; symbols are means, error bars are 2 standard errors.

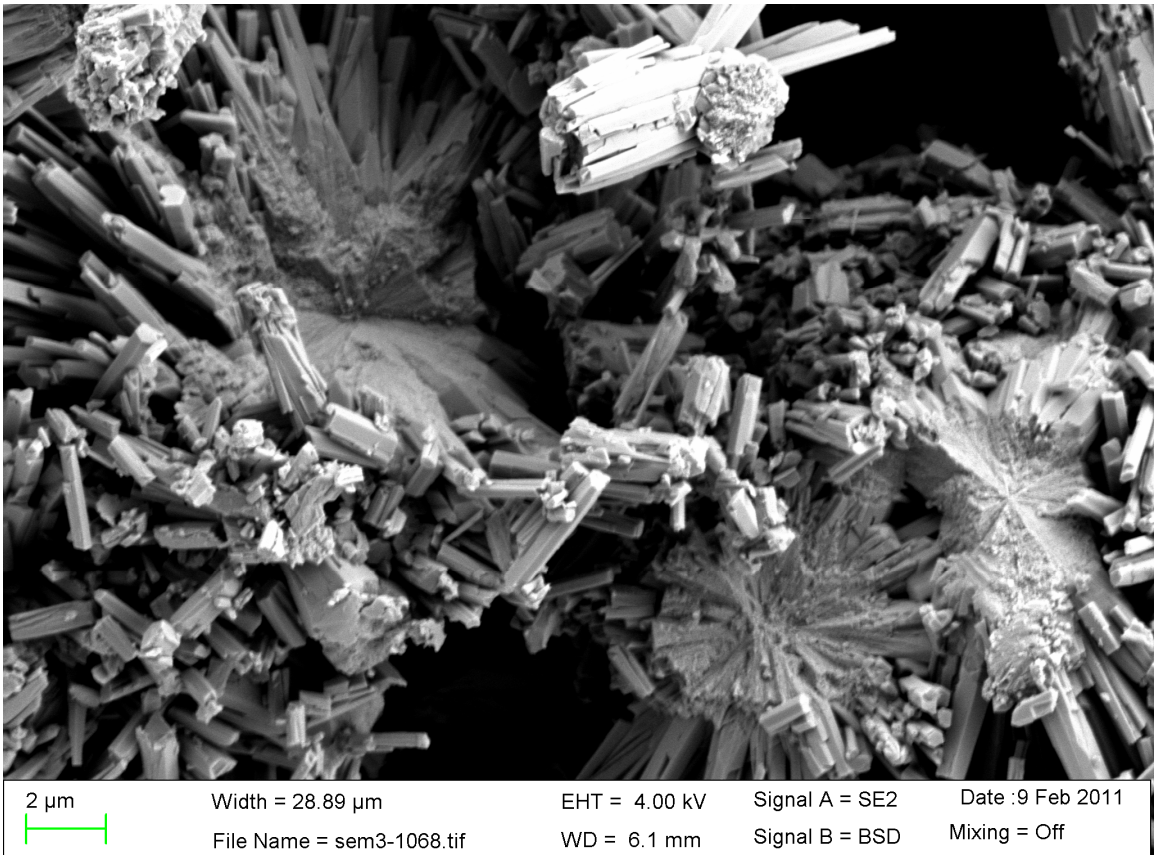
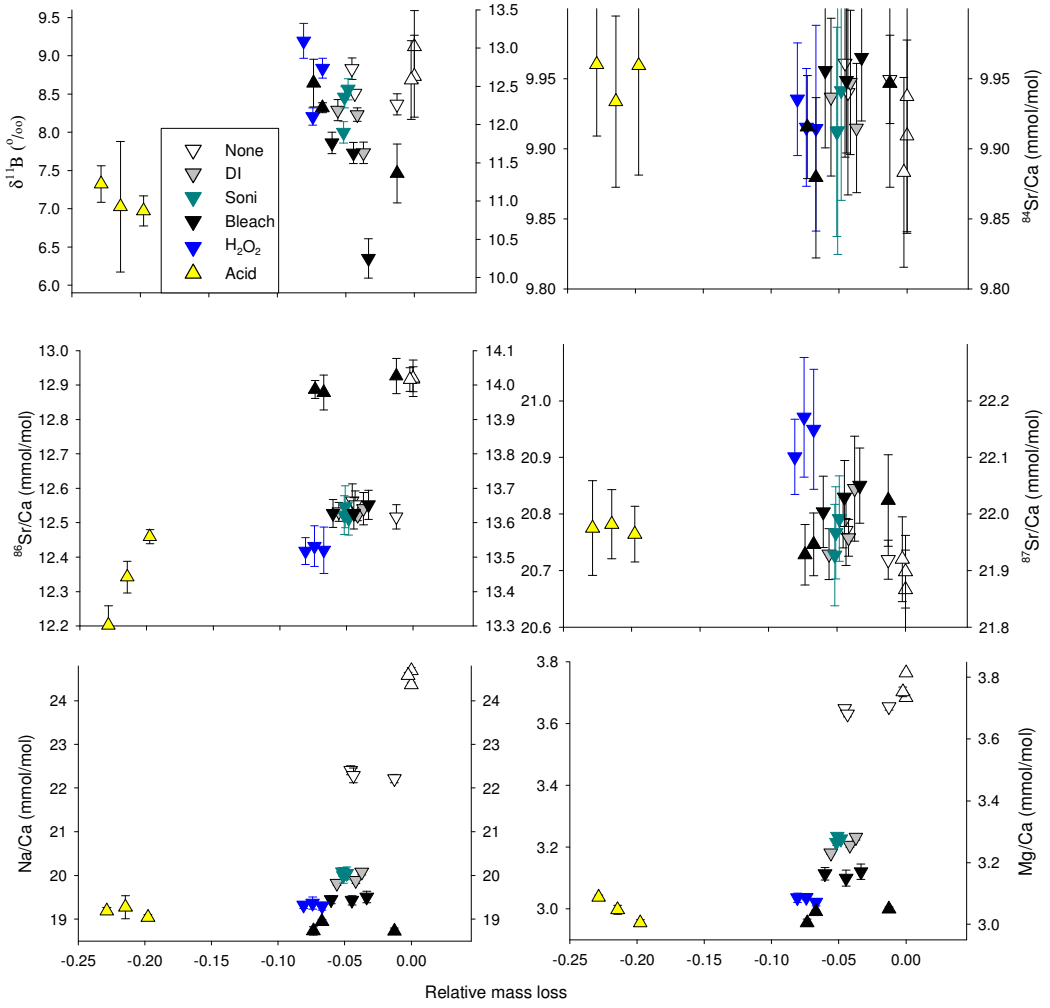



Figure S6. SEM image of precipitate 1/19/11 e. Note the relatively small crystal size and exposed nucleation sites.




1205

1206 Figure S7. Relative mass loss versus $\delta^{11}B$, $^{84}Sr/Ca$, $^{86}Sr/Ca$, $^{87}Sr/Ca$, Na/Ca, and Mg/Ca

1207 for synthetic aragonites. Up triangles represent 1/19/11 e (plotted on the axis to the right

1208 of each plot), down triangles 1/19/11 d (plotted on the left hand axis). Different

1209 treatments are shown in different colors. Error bars are the greater of 1 standard

1210 deviation for repeated measures of a given sample, or the measurement standard

1211 deviation for trace element measurements. For boron isotopes, error bars are 1 standard

1212 deviation of repeated measures of the given sample, or if only one measurement was

1213 made, the average standard deviation was used.

1214

A supplemental data file containing data associated with each figure is available (Supplemental file cleaningpapersupplement.xls).